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# HYDROCARBON PROCESSING<sup>®</sup>

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**Cover Image:** Close up industrial view at oil refinery plant from industry zone.

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## Despite reaching \$180 B, new project announcements are down year-over-year

Over the past year, the Global Energy Infrastructure (GEI) database has tracked more than \$180 B in new project announcements. Most of these investments (approximately \$70 B) are in the Asia-Pacific region. This region continues to invest heavily in all sectors of the hydrocarbon processing industry to satisfy increasing demand for transportation fuels, petrochemical products and natural gas. Asia is followed by the Middle East and Eastern Europe, Russia and the Commonwealth of Independent States (CIS) region.

The following are total capital expenditures from new project announcements over the past year broken out by region:

- Africa: \$4 B
- Asia-Pacific: \$70 B
- Canada: \$18 B
- Western Europe: \$3 B
- Eastern Europe, Russia, CIS: \$30 B
- Latin America: \$1 B
- Middle East: \$40 B
- U.S.: \$15 B.

New project numbers have declined approximately 16% year-over-year. In 2021, the GEI database registered 205 new project announcements; however, that number decreased to just over 170 this year. The Asia-Pacific region accounted for most new project announcements in 2022, representing 37% market share. Asia was followed by Eastern Europe, Russia and the CIS. **Note:** This year, approximately half of the new project announcements in the region were in Russia. With increased sanctions against Russia due to its attack on Ukraine, it is very likely that capacity additions (e.g., LNG export terminal buildout, additional chemicals production) will be delayed or possibly canceled. However, only time will tell if these projects move forward, are delayed or abandoned. **HP**

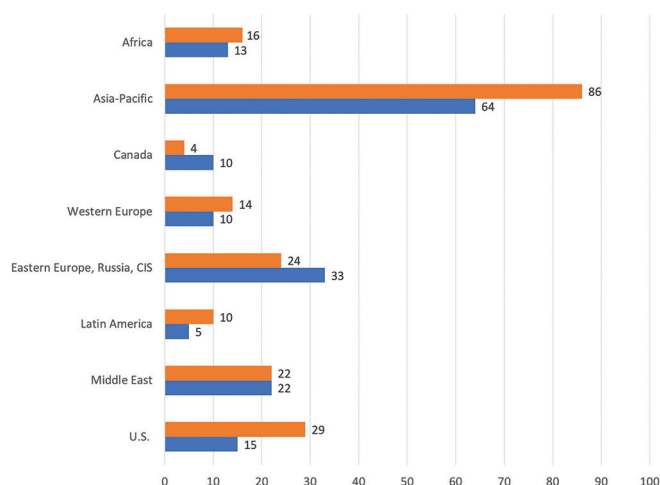


FIG. 1. New project announcements, 2021 (orange) vs. 2022 (blue).

# The Top Projects winners of 2022 have been announced

Each year, *Hydrocarbon Processing* honors the top refining and petrochemical projects of the year. These capital investments have significantly contributed to the expansion of the hydrocarbon processing industry and have been instrumental in providing new refined and petrochemical products to traditional and emerging markets.

Using Gulf Energy Information's Global Energy Infrastructure database, our editors select several capital projects in each sector as finalists for the Top Projects award. Once selected, readers of *Hydrocarbon Processing* can vote on the top project in each sector.

This year, the editors announced 10 nominees—five refining and five petrochemical projects—for this prestigious award. This year's nominees represented nearly \$50 B in capital investments, more than 600,000 bpd in new refining capacity and more than 11 MMtpy in additional petrochemicals production.

Over the past 2 mos, hundreds of readers voted online to select the top refining and petrochemical projects of 2022. Unlike previous years, both categories had ties. Despite extending voting times, the outcomes in both categories remained the same. Therefore, for the first time ever, there are two Top Project winners in both the refining and petrochemicals categories.

**Top Project: Petrochemicals.** The following projects have been selected as the Top Projects in the petrochemicals category in 2022:

- **LyondellBasell's propylene oxide (PO) and tertiary butyl alcohol (TBA) complex** (Channelview, Texas, U.S.): The nearly \$2.5-B project consists of two plants to produce 1 MMtpy of TBA and 470,000 tpy of PO.

Once completed in Q1 2023, the complex will be the largest PO/TBA complex in the world.

- **Long Son Petrochemicals complex** (Ba Ria-Vung Tau province, Vietnam): The \$5.4-B complex will produce nearly 1 MMtpy of ethylene, as well as propylene, polypropylene and polyethylene, once operational. Despite a fire at the facility in September, the complex's completion is still scheduled for 2023.

**Top Project: Refining.** The following projects have been selected as the Top Projects in the refining category in 2022:

- **Indian Oil Corp. Ltd.'s Barauni refinery expansion (BR9) project** (Begusarai District, Bihar, India): The nearly \$1.8-B project will expand the Barauni refinery by 3 MMtpy to 9 MMtpy. Once completed in Q2 2023, the upgraded refinery will produce transportation fuels that adhere to India's Bharat Stage-6 fuel standard.
- **Neste's Singapore refinery expansion project** (Singapore): The company is investing nearly \$1.5 B to expand its Singapore refinery. The project—to be completed by Q2 2023—will add 1 MMtpy of sustainable aviation fuels production, as well as renewable raw materials for polymers and chemicals production.

*Hydrocarbon Processing* would like to congratulate the winners of the 2022 Top Projects awards, as well as its global readership that participated in voting for this year's winners. **HP**

## INSIDE THIS ISSUE

**14 Catalysts.** New catalyst technologies are advancing refining and petrochemical processing. This month's Special Focus section features the latest catalyst technologies that are helping refiners produce clean fuels while adhering to strict emissions regulations.

**48 Process Optimization.** State-of-the-art sulfur recovery technologies utilize the modified Claus process as well as some extension technology on the tail gas. This article details a proprietary sulfur recovery process, whereby sulfuric acid produced in a wet gas sulfuric acid tail gas treating unit is recycled back to the Claus thermal reactor.

**55 Refining-Petrochemical Integration.** Fluid catalytic cracking (FCC) has become the second major propylene production technology after steam cracking, showing high flexibility in feedstocks and product distribution. This article details a novel FCC process that uses proprietary catalysts to selectively crack various heavy feedstocks to light olefins.

**64 Pumps.** Pump manufacturers and end users consider the pump warm-up system configuration to be an essential consideration during pump design, manufacturing and commissioning stages. The scope of this article focuses on typical guidelines and best practices for hot applications where warm-up systems are required for proper startup and reliability of the pump.



## Quality in construction: Taking a holistic approach

When it comes to quality in construction projects, it is easy to focus only on materials and installation—it makes sense that high-quality components lead to a high-quality end product. However, considerations such as process and scheduling can also have a significant effect on quality outcomes.

In the past, achieving quality on a project was synonymous with passing a test. In recent years, the definition of quality has broadened. Because the end goal of a facility owner is to have a successful turnover, with complete documentation and full readiness for production on day one, projects meeting these criteria are the ones that represent quality. Requests for proposals (RFPs) tend to focus on a project's description and scope in its strictest sense, leaving out ancillary—but important—considerations that can go on to become “hot button issues” once the project is underway. To prevent this, planning, design and construction teams should strive to understand the facility's operating unit, even before ground is broken. Early conversations that specifically address operational concerns will allow the delivery of an optimally functioning facility.

A case in point is addressing quality in decisions surrounding materials, access and installation complexity. For example, whereas a safe, functional weld on a pipe can be said to represent quality, if choosing bolts would result in simpler, faster installation, then making that choice should be considered part of achieving quality on the project. Tie-ins to existing infrastructure are another critical consideration that benefit from early discussions. Most hydrocarbon construction projects have multiple points at which other plant operations will eventually feed into the system; therefore, the logistics of these tie-ins must be considered in advance, even down to delivery dates and locations, so that operations personnel in the existing facilities know what to expect and can schedule maintenance and other activities in a way that avoids conflicts. As with materials, access and installation complexity, project quality associated with tie-ins can be improved by talking through efficiencies with the project designer. For example, decisions about where to cut a pipeline for a tie-in should be made in a way that reduces the amount of support required for the remaining run of pipe. In addition, if a valve or other element will be installed in that spot and requires access, it should be determined in advance how the operator (and the contractor) can access it.

Issues such as testing and cleaning methods may seem like late-stage concerns, but leaving these details until the last minute can result in delays that cause extra days of plant shutdown and, potentially, millions of lost dollars. The team should agree from the outset what testing will be required

as part of the project's completion. Time-saving solutions include identifying locations where X-ray testing can be performed on pipe connections in just a couple of hours vs. procedures that would require setting up scaffolding and evacuating the pipe, which might take days. Ease of maintenance should also be considered during the design phase.

Not only does quality pertain to a facility's functionality beyond just materials and installation, but, for hydrocarbon projects, quality encompasses life, health and safety concerns that far exceed those associated with many other types of construction. There is a risk, for example, of toxic gasses escaping the system during integration of the infrastructure—this can include a risk of explosions. For this reason, it is especially critical to involve individuals outside the usual chain-of-command when making decisions such as shut-off scheduling.

There is another benefit to thinking of quality as a process rather than an outcome that can be measured with a simple test: a facility owner's company culture, as well as employee satisfaction, can be positively impacted. Instead of allowing personnel outside of the construction team to remain siloed, making them part of the conversation and addressing their expectations and concerns makes them feel valued and helps them bond to others within the organization. Experienced site representatives for the construction company can facilitate conversations between facility operators and corporate decision-makers. Having contractors conduct site visits during the estimating and procurement stages is also a good way to communicate with plant operators regarding work schedules and logistic needs for the mutual benefit of all parties.

**Tools that guide quality.** A project's delivery method can also influence quality. Traditional design-bid-build—in which a facility's design is completed and then sent out to bid—hampers the ability to accomplish front-end planning. Failing to capture the insights that result from early planning can have a devastating impact on a project's profitability or even its constructability if the discovery of unfeasible project elements happens too late to be mitigated.

Just as adhering to prescribed installation processes and procedures ensures quality in physical workmanship, adhering to construction management processes ensures quality in overall project outcomes. Fundamentals include keeping a good paper trail, proactively managing project cost and schedule, and hiring only qualified workers. From a big picture point of view, the preconstruction team should view every aspect of a project as a potential for continuous improvement. They should direct capital toward the areas that best benefit the organization's overall goals. Each step in the capi-

tal process should be connected to and build upon the previous step. Quality benchmarks should be established early and audited along the way.

The Construction Industry Institute (CII), a consortium of more than 140 leading owner, engineering, contractor and supplier firms, created a tool known as the Project Definition Rating Index (PDRI), which guides project scoping and

planning. It was developed based on an analysis of more than 25,000 completed capital projects and helps teams identify and define project elements prior to detailed design and construction. This, in turn, leads to the early recognition of risk factors related to cost, schedule and operating performance.

The PDRI consists of a weighted scoring system whereby a preconstruction team can assign a rating to various key elements of an industrial facility project. The result is a final score that indicates the overall risk associated with a project, helping direct risk mitigation efforts and even indicating whether a project is viable. It aligns the expectations of team members and owners, allowing them to transition smoothly through the design and construction phases and into effective startup and operations. Using a system such as the PDRI provides the project team with a detailed checklist for work planning, standardization of scope definition and terminology, assistance in monitoring progress, help in communicating requirements among participants, a method for reconciling differences among project participants, and a training tool.

Cost and schedule issues have a way of turning into physical problems. Therefore, teams should define quality as a project's ability to fulfill its intended purpose, be executed safely, and meet budget and schedule requirements. Quality is not simply an outcome; it is a process. Early collaboration among team members to "design in" construction and scheduling efficiencies ensures smoother project turnover and, eventually, better plant operations. **HP**



**FIG. 1.** Achieving quality in hydrocarbon construction projects includes addressing decisions surrounding materials, access and installation complexity.

## New series of high-strength austenitic stainless steels

N'GENIUS Materials Technology has developed a new series of high-strength austenitic stainless steels that the company says will transform how materials are specified and utilized across the oil and gas sector.

The N'GENIUS Series™ has been specifically developed to out-perform, supersede and supplement the majority of existing grades in the 300 Series, the corrosion resistant alloy (CRA) line pipe grades now available for selection in the API Specification 5LX and the DNV-ST-F101 standard, plus the CRA Oil Country Tubular Goods (OCTG) in the API Specification 5CT for Casing and Tubing.

The company states that the range of alloy types, variants and grades in the N'GENIUS Series have strength properties equivalent to duplex and superduplex stainless steels, and ductility and toughness levels normally associated with conventional austenitic stainless steels, but with superior corrosion resistance to suit all major oil and gas projects.

Key engineering design characteristics will allow a range of product forms and ancillary equipment to be designed, specified, manufactured and supplied with the objective of reducing wall thicknesses and overall size, using less material and producing lighter products. This makes products easier to manage and transport to site, leading to weight savings, an overall reduction in construction and project costs and—perhaps most importantly—contributing to lower carbon emissions.

The company states that the N'GENIUS Series fulfils the need for CRA pipeline material that satisfies all requirements of design engineers, process engineers, corrosion specialists and project engineers for major CRA pipeline projects in a wide range of service conditions, including high-pressure, high-temperature (HPHT) developments and process media environments containing

various levels of chlorides, CO<sub>2</sub>, H<sub>2</sub>S and other constituents. The N'GENIUS Series also ensures resistance to hydrogen embrittlement and, in particular, stress corrosion cracking (SCC) in aggressive media environments.

## Rupture disk improves process performance and efficiency

OsecoElfab has launched its LoKr reverse rupture disk (FIG. 1) for chemical process and petrochemical plants. The new disk design delivers a best-in-class flow resistance factor, or KR, to maximize pressure relieving performance while delivering superior reliability and service life.

The disk's architecture has been refined and optimized to improve performance in three key areas: keeping pressure drops in relief lines to an absolute minimum; providing maximum reliability and accuracy; and being suitable for the widest range of pressures, temperatures and line sizes possible.

The reverse-buckling disk combines a dimple on the disk with a knuckle on the holder to offer full-bore opening with exceptionally accurate burst ratings. This enables a higher flowrate on burst than previously possible, demonstrated by the disk's low KR value of 0.22. This makes it easier to keep pressure drops across the relief line below 3%, when the LoKr is used in relief valve isolation. Process plants can continue to use smaller piping diameters with no loss of performance or efficiency, even at low flowrates. Designed to ASME XIII standards and certified with a UD stamp at a best-in-class KR value of 0.22, the LoKr is now available.

## New line of differential pressure gauges

Marsh Instruments has introduced a new line of differential pressure gauges (FIG. 2). These devices measure the difference between two inlet pressures in a system using just one instrument, and can

help extend equipment life and prevent malfunction. These are the first differential pressure gauges backed by Marsh Instruments' century-and-a-half reputation as the standard of accuracy.

Diaphragm-type and piston-type differential pressure gauges are in stock and available to ship now through authorized distributors. Other configurations will be rolled out soon, and can also be manufactured to specific customer demand.

Options include aluminum or 316SS wetted parts; multiple dial sizes of 2.5 in., 4 in., 4.5 in. and 6 in.; static pressures up to 6,000 psi; inline, bottom or back connections/ports; and direct, front flange, 2-in. pipe and surface mounting. Maximum/minimum pointer and integrated pressure switches are also available.

Differential pressure gauges from Marsh Instruments can detect clogs, flow abnormalities and help determine proper system functioning in diverse applications such as oil and gas, irrigation, HVAC and filtration, as well as measure liquid levels in cryogenic tanks. Large-dial versions are available for use on backflow prevention and test applications in municipal water systems.



FIG. 1. OsecoElfab's LoKr reverse rupture disk for chemical process and petrochemical plants.



FIG. 2. Marsh Instruments' new line of differential pressure gauges.



## Catalyst shaping technology

BASF has introduced its novel X3D™ technology, a new additive manufacturing technology for catalysts based on 3D printing. Catalysts produced with this technology feature an open structure, resulting in a reduction of pressure drop across the reactor and a high surface area, significantly improving the catalysts' performance. BASF has capabilities to supply commercial quantities.

The technology offers a greater freedom of catalyst design compared to conventional production technologies. It brings catalysts' performance to the next level and helps to customize catalysts to customers' specific conditions and needs by designing infill pattern, fiber diameter and orientation. Customers can benefit from an increased reactor output, higher product quality and lower energy consumption. The novel catalysts are mechanically robust and proven in commercial plant operation externally and for several years in BASF.

BASF can apply the technology to a wide variety of existing catalytic materials, including base or precious metal catalysts, as well as carrier materials. BASF's sulfuric acid catalysts O4-111 X3D and O4-115 X3D are the first catalysts produced with the new technology and are used in industrial plants.



**FIG. 3.** NETZSCH Pumps North America LLC has released its new TORNADO® T1 pump.



**FIG. 4.** Emerson's DeltaV™ IO.CONNECT subscription software service.

## Rotary lobe pump produces high flow in a compact package

NETZSCH Pumps North America LLC, an expert in solutions designed specifically for difficult pumping applications, has released its new TORNADO® T1 pump (**FIG. 3**), designed to produce high flow at low-to-medium pressures in a small compact package. It is ideal for applications in biogas and biomass plants. The TORNADO T1 pump can handle a wide range of viscosities, solids, temperatures, abrasions, and corrosive/acidic process fluids and environments.

The TORNADO T1 pump is versatile for just about any orientation and installation. Its robust design offers longevity, operational flexibility and dry-run capabilities, allowing the pump to operate and handle many upset process conditions without causing harm to the pump. The pumps are available up to > 4,000 gpm and up to 130 psi.

The NETZSCH TORNADO T1 is a Full Service-in-Place (FSIP®) pump. The front pullout design allows for easy access for maintenance and inspection. Opening the front cover allows access to the wear plates, lobes and seals, making this pump easy to service. Additionally, there is no need to access the timing gears or bearing as they are protected with the NETZSCH Gearbox Security System (GSS). The GSS is an air gap that exists between the mechanical seal and the lip seal of the timing gearbox that establishes a physical separation between them and protects the gearbox from the process side of the pump (wet-end). Should the mechanical seal leak, no product can get into the pump's gearbox to contaminate the timing gear oil. The air gap allows for the process fluid to drip away from the shaft and timing gearbox to prevent damage; the process fluid physically cannot pass through the air gap and migrate past the gearbox lip seal. This air gap fully prevents the intermingling of the two fluids, resulting in improved long-term operation and lowering total cost of ownership. Repairing bearings, lip seals and timing gears are greatly diminished with the TORNADO T1 rotary lobe pumps.

New upgrades include improved flange sealing, a one-piece housing design, additional seal configurations (single, double, flush, quench, etc.), a superior wear plate,

and newer materials and coatings that extend operation life.

## I/O interface software helps future-proof operations, reduce modernization costs

Emerson has released DeltaV™ IO.CONNECT, a new subscription software service designed to help plants simplify modernization with an open architecture pathway to more efficient control schemes without the need to completely overhaul existing infrastructure (**FIG. 4**). In a traditional plant with tens of thousands of I/O points and many controllers, this can save hundreds or thousands of hours of labor and up to 40% of the capital required for a total rip-and-replace upgrade.

Many plants still using control systems from 20 yr–30 yr ago are unable to reap the benefits of modern, digital technologies that optimize operations and improve sustainability. Modernizing those systems is complicated by the extensive time, labor and capital expense required to convert the old wiring, terminations and other infrastructure they are built upon, leaving plants “locked in” to legacy control technologies.

DeltaV IO.CONNECT provides a faster, easier and more cost-effective path to replacing any legacy system with a new DeltaV distributed control system while leaving existing I/O infrastructure in place. The solution is provisioned as a subscription software component of Emerson's Guardian™ Support offering, helping plants drive strategic goals and meet business needs with future-proof operation. No legacy vendor software is required for the configuration and maintenance of I/O.

By preserving existing I/O and leaving wiring intact, plants can reduce new system transition time by > 90%, keeping production on pace, reducing risks and minimizing downtime. Once the interface is installed and the plant is running new control technologies, technicians can update I/O on their preferred schedule while the plant runs, shifting what used to be a capital expenditure to the operations budget and driving immediate return on investment through improved process control performance. **HP**

An expanded version of Innovations can be found online at [www.HydrocarbonProcessing.com](http://www.HydrocarbonProcessing.com).

## Creating trusted environments



**FRANK SANJAY** is the Manager of the Product Cybersecurity Center of Excellence at Eaton, and a member of the ISA Global Cybersecurity Alliance. He helps customers by driving Eaton's "Secure by Design" philosophy in various intelligent products, providing technical guidance to global product engineering teams for implementing cybersecurity. Sanjay leverages hard-earned practical expertise from more than 17 yr of hands-on cybersecurity assessments, technology risk management and leading highly technical cybersecurity teams.

*Hydrocarbon Processing (HP)* sat down with Frank Sanjay (**FS**), Manager of the Product Cybersecurity Center of Excellence at Eaton, an intelligent power management company. In this interview, Sanjay discussed why addressing cybersecurity risks is imperative for downstream refining and petrochemical industries, as well as how to focus on supply chain cybersecurity, leveraging emerging cybersecurity standards to mitigate risk.

**HP:** What are some of the key lessons to learn from recent cyber incidents?

**FS:** We see malicious cyber activities increasing. New vulnerabilities are discov-

ered every day and having strong cybersecurity protections may not be enough when attackers shift their attention to suppliers. The security of a network or a system is only as strong as its weakest link.

I'd like to underscore two critical lessons from recent cyberattacks: first, people are typically the weakest link when it comes to cybersecurity; and, secondly, the likelihood of a cyberattack is grossly underestimated.

The investigative report of a recent pipeline breach revealed that attackers exploited an employee's compromised credentials. The employee was using the same credentials for the corporate network and his personal account. The personal account was compromised and the pipeline attackers gained access to that information and abused it, eventually halting operations.

The mistaken belief that cybercriminals need to possess highly sophisticated skills results in underestimating the likelihood of a cyberattack. It is often forgotten that highly sophisticated hackers are monetizing their skills, offering malware that can discover vulnerable networks and selling devices accessible on the internet. Malicious actors are building tools that significantly lower the bar for the technical skills needed to carry out a cyberattack. A recent advisory by the Cybersecurity and Infrastructure Security Agency (CISA) warns about the industrial control systems attack framework Pipedream, underscoring the rising cyberthreat to the energy sector around the world.

**HP:** What does the hydrocarbon processing industry (HPI) need to change in response to recent cyber incidents?

**FS:** Executive attention is needed because cyber risk is not just technology risk—it is a business risk. Traditionally, cybersecurity has been treated as a technology problem, and information technology (IT) teams often have the respon-

sibility to mitigate cyber risks. However, cybersecurity goes far beyond IT.

At Eaton, we believe that cybersecurity must be viewed from an organizational perspective, just like quality and safety. Businesses must engage broader stakeholders, including operational technology (OT), supply chain, legal, finance, human resources and marketing functions. The implications for cyber breaches are far-reaching and wide, so it is important to plug security holes everywhere. IT teams cannot remediate this problem alone.

In many companies, cybersecurity is an afterthought. We need to treat cybersecurity and cyber threats as a risk to be managed and owned by organizations' senior leaders and supported by leaders at every level. Cybersecurity needs to be part of an overall corporate strategy and should be embedded deeply into organizational operations.

At Eaton, we have taken an enterprise-wide approach that promotes the highest level of defense against emerging cybersecurity threats. Cybersecurity is part of our DNA and an integral consideration, with protocols placed on the people, processes and technologies within our Secure Development Lifecycle (SDLC) process. The process integrates security checkpoints at various phases of product creation. Security within SDLC spans from inception through to deployment and maintenance, enforcing cybersecurity best practices via training, threat modeling, requirements analysis, implementation, verification and ongoing support.

**HP:** What are the major technology cyber risks?

**FS:** While many OT risks must be addressed, I believe organizations need to focus on a few critical areas.

First, ensure all remotely accessible network connections are managed securely. This starts with the discovery of all the remote access points into a company, the removal of unnecessary connections,

and securing the rest with multi-factor authentication, network segregation and authorization on a strict need-to-know basis. Detecting and protecting all remote connections requires both IT and OT staff to collaborate.

Second, while solutions entering the market are offering spectacular features for monitoring and managing OT environments, few provide any cybersecurity. Even worse, some of these technologies introduce new vulnerabilities when connected to already fragile OT environments. Cybersecurity experts should evaluate any new tool to effectively manage risks and determine capabilities.

Third, OT systems are fragile when it comes to cybersecurity and the patching of vulnerabilities. These systems may be many decades old and have limited or no ability to receive patches or updates. With each passing day, these kinds of systems become increasingly vulnerable. Organizations need a comprehensive cybersecurity strategy to manage legacy devices, update device configurations and regularly apply patches (to the devices that support patching). Further, organizations should implement an additional layer of protection for legacy devices that are critical to their operations.

Finally, OT environments often rely heavily on physical security controls, which are insufficient. Traditionally, OT systems may tolerate reuse and sharing of credentials, which creates risks. These credentials can be compromised externally and could compromise OT and IT operations. Therefore, having a comprehensive OT cybersecurity awareness program is important.

#### **HP: What role does the supply chain play in securing OT environments?**

**FS:** In the oil and gas industry, multiple vendors, contractors and asset owners are involved in projects. To ensure effective cybersecurity, it is important to have a clear understanding of the cyber risks, roles and responsibilities for each stakeholder. The supply chain management (SCM) team plays a critical role when procuring new equipment, services and vendors, and should be an integral part of cybersecurity processes. By involving cybersecurity experts to help manage risks when new solutions are considered, the supply chain management team can

help protect organizations from increasing cyber risks unknowingly.

#### **HP: What standards could support the efforts of securing OT environments?**

**FS:** Cybersecurity must be embedded within all processes and procedures throughout the lifecycle of any project implementation—from early concept studies to the decommissioning of equipment. Yet, there is no dedicated standard for the HPI.

That said, the International Society of Automation (ISA)/International Electrotechnical Commission (IEC) 62443 series of standards can be utilized effectively within processing industries in general and hydrocarbon processing specifically. The standards describe cybersecurity requirements. By using recommended practices tailored to the HPI, the following standards can be effectively applied:

- ISA/IEC 62443 Part 2-1 can be used to establish a security program and define requirements for how security needs to be considered.
- Organizations can use ISA/IEC 62443 Part 2-3 for patch management in OT environments.
- Applying ISA/IEC 62443 Part 2-4 can help establish security program requirements for service providers.
- Technical requirements can be established with ISA/IEC 62443 Part 3-3 to help secure systems.
- Importantly, vendors could be required to show compliance to standards like ISA/IEC 62443 Part 4-1, demonstrating their cybersecurity capabilities.
- Likewise, ISA/IEC 62443 Part 4-2 could be leveraged to ensure devices with appropriate cybersecurity capabilities are procured and deployed into environments.

Cybersecurity is a global threat. Creating trusted connected environments is critical. Mitigating cybersecurity risks requires an all-encompassing strategy involving people, processes and technology. Because cyber risks can creep into critical OT environments through vendor-supplied devices, systems, software and services, addressing supply chain risks is imperative for downstream refining and petrochemical industries. **HP**



## Catalysts

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## Solving maldistribution: Catalyst loading and why it matters

Are your reactor yields lower than forecast? Does your fixed-bed catalytic reactor suffer from hotspots? Are your cycle lengths shorter than planned? If you answered “yes” to any of these, then your reactor could be suffering from liquid/gas maldistribution—one of the most common causes of poor reactor performance.

The impact of maldistribution can be severe and long-lasting, yet its root cause is often misunderstood. Although faulty or poorly installed reactor internals are often to blame, maldistribution can be frequently traced back to poor catalyst loading.

The authors’ companies collaborated to share insights into the impacts of maldistribution and the critical role that catalyst loading plays in reactor performance, as well as the important steps that plant personnel can take to ensure optimal performance of expensive catalyst and hardware.

**Maldistribution: How is it affecting production?** Maldistribution is described as the preferential flow and the uneven distribution of liquids and/or gases within a catalyst bed, which can have the following consequences:

- Off-spec products due to the suboptimal use of the loaded catalyst volume
- Shorter-than-expected cycle length due to end-of-run (EOR) conditions reached sooner than expected
- Hotspot formations and the resulting threat to the mechanical integrity of the reactor.

**Performance impacts: Poor use of catalysts.** Ideally, the weight hourly space velocity (WHSV) should be uniform within the entire catalyst bed volume; however, if a reactor is suffering from

maldistribution, then portions of expensive catalyst are being underused (with a lower-than-average WHSV), resulting in lower-than-expected yields and off-spec products. Consequently, the reactor must run under more severe conditions to meet the targeted product properties or yields.

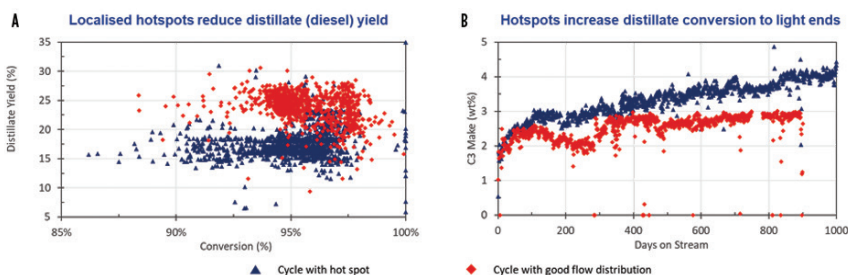
**Time impacts: Shorter run/cycle times and increased downtime.** In the most severe cases, maldistribution can lead to the early termination of the reactor cycle. This is caused by the development of hotspots—sections of the catalyst bed where the liquid/gas flow is impeded, causing high temperatures—that result in EOR temperatures being reached sooner than scheduled. Should a cycle be cut short, valuable run time is replaced with the costly and time-consuming process of replacing exhausted catalysts. In the most extreme cases, the hotspot temperature can be high enough to threaten the mechanical integrity of the reactor and cause severe safety incidents [e.g., reactor rupture, fire, explosion or hydrogen sulfide ( $H_2S$ ) release].

For example, imagine that plant personnel have targeted a 1,000-d unit cycle

length, but the development of maldistribution forces the cycle to terminate after only 730 d, thereby reducing cycle run time by 27%. Stopping the unit earlier than scheduled and taking up to 3 wk to load a fresh batch of catalyst can impact the bottom line by as much as \$18 MM (the cycle scenario assumes a planned yield quota of \$500,000/d, a total planned cycle revenue of \$500 MM, and replacement catalyst and downtime costs of \$18 MM).

**Cost impacts: Lost revenue and poor return on investment.** Maldistribution results in lower yields, shorter cycles and more downtime, which, together, have a significant impact on unit economics by increasing the total cost of ownership (TCO) of each reactor (FIG. 1). Moreover, each cycle requires an investment in catalyst, hardware, feed and labor, which is calculated based on the forecast yield. If the yield is down and downtime is up, then return on investment (ROI) will be lower. The impacts of maldistribution are unpredictable, and unpredictability is difficult to budget.

**Spotting maldistribution: It is all in the temperature.** The key to identifying



**FIG. 1.** The presence of hotspots (A) that can reduce distillate (diesel) yield. Localized hotspots (B) can lead to over-cracking and the conversion of desired products (e.g., distillates) into undesirable light ends.

maldistribution is monitoring and understanding temperature variations in the catalyst bed (FIG. 2A). The development of hotspots is an important indicator that a reactor is suffering from maldistribution.

Hotspots are problematic, as they increase the weighted average bed temperature (WABT) of a catalyst bed. This results in the EOR temperature being reached sooner than expected, and the early termination of the catalyst cycle life.

The pattern (or distribution) of hotspots provides valuable information about the probable cause of maldistribution (FIG. 2B). For example, if the whole north side of a reactor is hotter than the south side, this suggests that the north (hotter) side is experiencing restricted liquid/gas flow, while the south (colder) side experiences higher liquid/gas flow, possibly because of a tilted catalyst bed

surface or a tilted internal component, such as a distribution tray.

**What is (really) causing your maldistribution?** The first response of most reactor operators whose units are suffering from maldistribution is to think that their hardware is to blame. For example, they may assume that their distribution trays have not been installed properly or that they are faulty. However, more often than not, the problem does not lie in the hardware, but somewhere many do not look: in the quality of the catalyst loading.

Catalyst loading controls four key variables that are central to the liquid/gas flow and thermal characteristics of a catalyst bed: the density, homogeneity, profile of the catalyst bed and the catalyst integrity. Get any of these wrong and, no matter how robust the processes are or how well

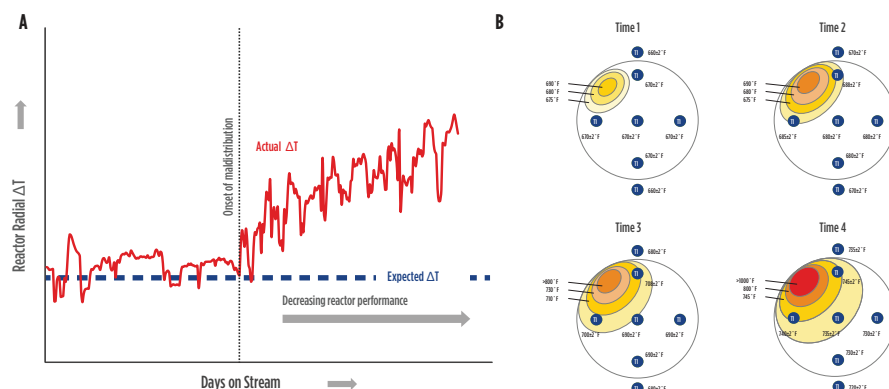
the hardware is performing, the reactor will likely suffer maldistribution and reduced performance.

Even with industry-leading distribution trays that offer near-perfect catalyst wetting (FIG. 3), poor-quality catalyst loading can reduce the performance advantages offered by optimized distribution hardware.

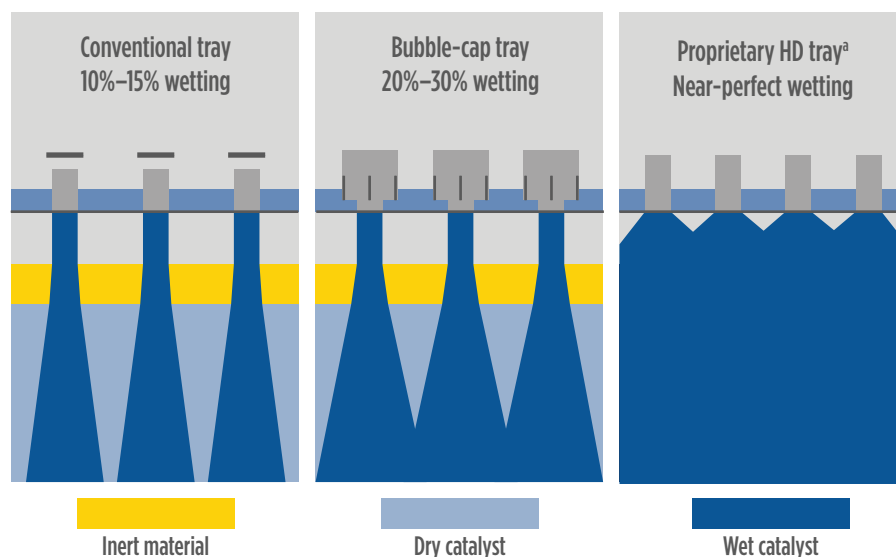
**Low average catalyst bed density.** The average density of the catalyst bed describes how tightly individual catalyst particles are packed together throughout the entire bed (FIG. 4). If the average density of the bed is too low, then the total mass of the loaded catalysts will be lower, resulting in reduced overall catalyst activity.

**Low homogeneity.** Homogeneity describes how the localized density of the catalyst bed varies throughout its volume. Low homogeneity reflects significant localized density variations, even if the average density of the bed meets expectations. If local density varies, then fluids will preferentially flow through lower-density zones, thereby leaving higher-density zones poorly utilized and prone to the development of hotspots. Moreover, WHSV is lower than average in high-density zones, while it is higher than average (not to say significantly higher) in low-density zones.

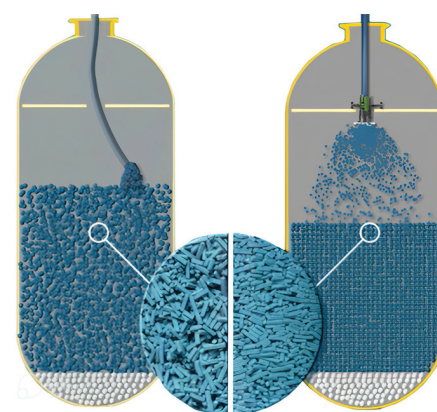
**Poor catalyst integrity.** Catalyst integrity describes the extent to which catalyst particles remain intact during loading. Broken catalyst particles form fines and dust that plug the interstitial space between particles, and prevent liquid and gas from freely and homogeneously circulating between all catalyst particles. Increases in lo-



**FIG. 2.** Onset of maldistribution shown by increasing and more variable radial  $\Delta T$ s (A). Maldistribution may cause localized hotspots to form, resulting in high radial  $\Delta T$ s (B).



**FIG. 3.** Well-designed distribution trays can offer near-perfect catalyst wetting, essential for optimal liquid/gas distribution.



**FIG. 4.** Poor-quality catalyst loading results in poorly aligned catalyst particles (left), larger void spaces and a lower total mass of the loaded catalysts. High-quality catalyst loading (right) results in well-aligned catalyst particles, smaller void spaces and a higher total mass of loaded catalysts.

cal density, caused by fines and dust, can also lead to higher pressure drops across the catalyst bed, which can significantly affect the reactor catalyst cycle length.

**Uneven bed profile.** If the top surface of the catalyst bed is tilted or uneven, then liquid/gas will preferentially converge toward the lowest point of the top surface and create a preferential flow path (**FIG. 5**). This will occur even if the overlying distributor trays are well-installed, perfectly leveled and running optimally.

**What controls the quality of catalyst loading?** The quality of catalyst loading is ultimately controlled by two key factors: operator's mindset and technology choice.

**How an operator's mindset impacts catalyst loading.** When considering the most important factors that determine reactor performance, most operators will list their operational processes, the reactor internals and the catalyst as their star performers. However, the importance of catalyst loading is often overlooked, despite the significant impact it can have on reactor performance.

When it comes to catalyst loading activities, most refiners want to have them executed as fast as possible and at the lowest possible cost. According to the authors, as many as 90% of refinery personnel are uninformed about the signs, causes and impacts of poorly loaded catalyst; this is a conversation that commonly only happens when a reactor is already suffering liquid/gas maldistribution.

**How technology choice impacts catalyst loading.** The desire for cheap and quick catalyst loading often dictates the choice of loading technology. Two methods are in widespread use: sock loading and dense loading.

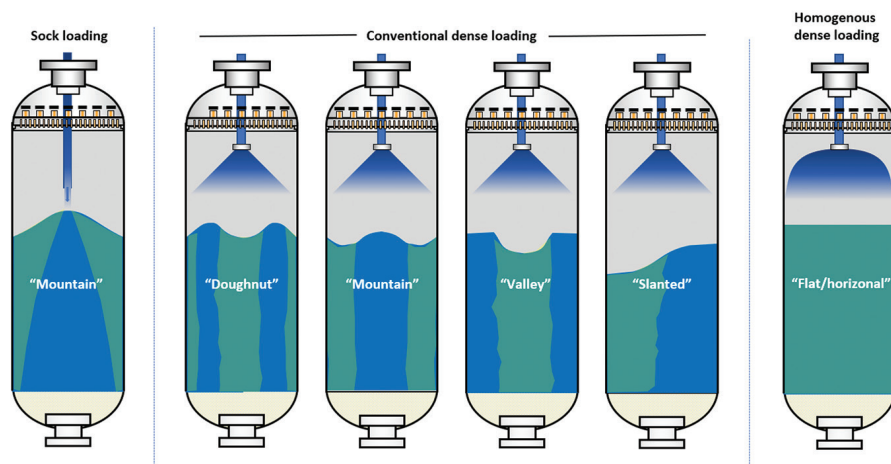
**Sock loading.** Sock loading involves the loading of catalyst via a large canvas tube (**FIG. 5**) and is the favored method for operators looking for a low-cost loading solution. However, despite its relatively low cost, sock loading has the following significant drawbacks:

- **Low homogeneity:** Improper settling and non-homogeneous distribution of catalyst particles make the catalyst bed vulnerable to differential compaction as particles shift and void spaces collapse under the weight of overlying catalyst. This leads to the formation of localized pockets of higher-density packing and inhomogeneities that promote the development of liquid/gas maldistribution.
- **Uneven profile:** Because sock loading only distributes particles over a narrow area, catalyst handlers are required to work inside the reactor to direct the sock. However, despite their best efforts, the result is invariably poor catalyst distribution, a tilted or uneven top catalyst surface, and

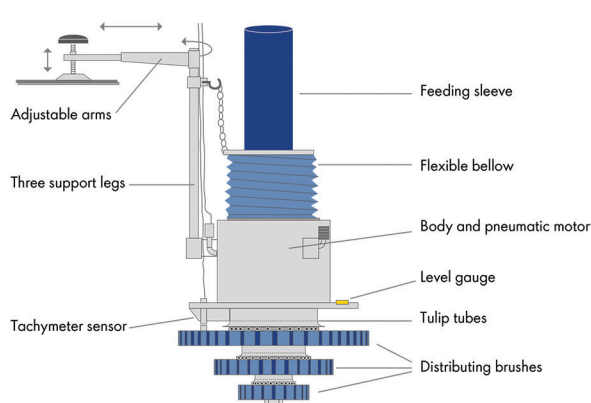
inhomogeneities caused by the trampling of catalyst underfoot.

**Conventional (lower-quality) dense loading.** Conventional dense loading (CDL) involves the distribution of catalyst in a rain-like fashion from a particle dispenser lowered through an overlying manway. As the catalyst is allowed to fall freely, the particles settle in a more stable and uniform way, thus increasing bed density and homogeneity. Yet, although CDL technologies—some of which are decades old—are generally superior to sock loading, they also have drawbacks:

- **Poor catalyst integrity and inhomogeneity:** CDL technology typically uses a set of rapidly rotating whips to propel catalyst outward, forming a diverging shower of particles. However, the whips are very aggressive, and



**FIG. 5.** Sock loading and conventional dense loading often lead to an uneven catalyst bed top surface that channels fluid flow through preferential zones (light blue shading). High-quality homogeneous dense loading creates a flat top surface that, in combination with optimized distributor trays, enables even wetting of the catalyst volume.



**FIG. 6.** HDL technology (left) is designed to load catalyst at the optimal rate and disperse particles, using centrifugal force gently and evenly across the full diameter of the catalyst bed (right).



they reduce catalyst integrity by breaking the catalyst into shorter (finer) particles that settle in denser, random arrangements, resulting in inhomogeneities. This impact is greater in larger reactors where greater forces are needed to propel the catalyst over longer distances to the reactor walls.

- **Uneven profile:** The most widely used conventional dense-loading machines often suffer from irregular distribution and suboptimal load rates, and lack the power to propel catalyst to the edges of the reactor—a problem amplified in larger units. This results in uneven mountain, doughnut or valley surface profiles that generate preferential flow

channels (FIG. 5). To prevent this, personnel are frequently required to climb inside the reactor to redistribute the catalyst.

- **Space restriction:** Whip mechanisms require more vertical and radial space to operate, which makes them difficult to deploy in smaller-diameter reactors. Moreover, they enable catalyst to be loaded only to 70 cm (28 in.) below the overlying distribution tray; a sock is then needed to finish the loading to the required elevation.

Moreover, CDL is unable to compensate for the shadow effects caused by installed hardware, such as thermocouple support structures, vertical quench and catalyst dump pipes. The shadow effect caused by these structures will of-

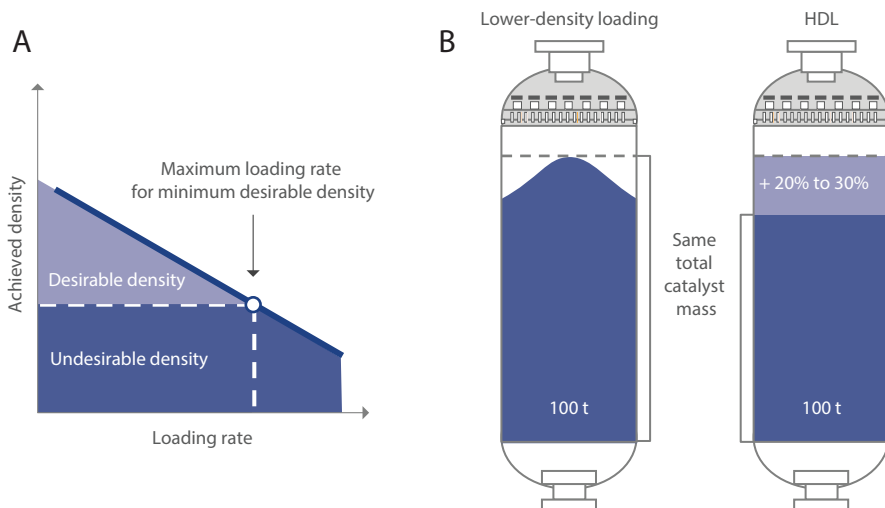
ten lead to maldistribution due to variations in bulk density in the vicinity of the installed hardware.

**Homogeneous (high-quality) dense loading.** Homogeneous dense loading (HDL) with an advanced catalyst loading method<sup>b</sup> operates on the same principles as CDL, but provides a significantly higher quality of loading due to a unique catalyst-distributing mechanism that relies on centrifugal force and brushes to distribute catalyst gently and evenly across a range of reactor sizes: from less than 0.5 m to more than 8 m (19 in. to 26 ft) in diameter (FIG. 6).

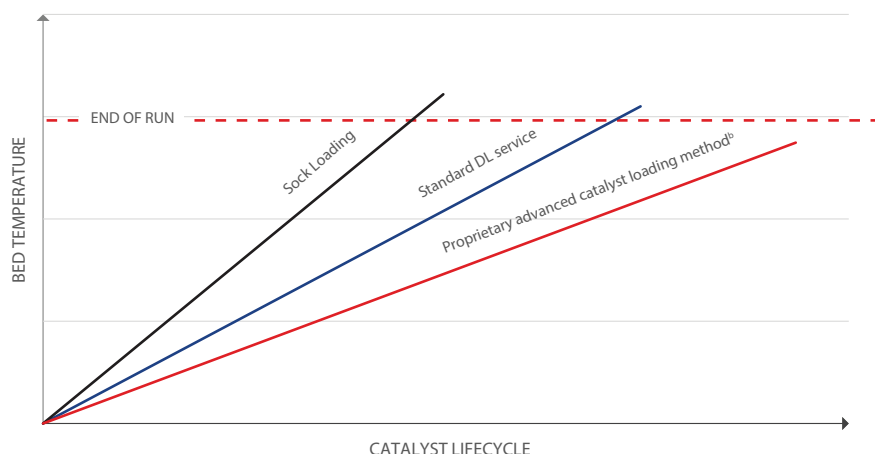
HDL can also minimize the shadow effects of internals when used with optimally designed hardware. For example, optimized internals can minimize the shadow effects of the hardware installed within the catalyst bed, which helps minimize the risk of liquid/gas maldistribution. Using leaner hardware with large and easy-to-open manways also facilitates higher-quality and faster loading.

HDL has many advantages over sock and CDL methods, including:

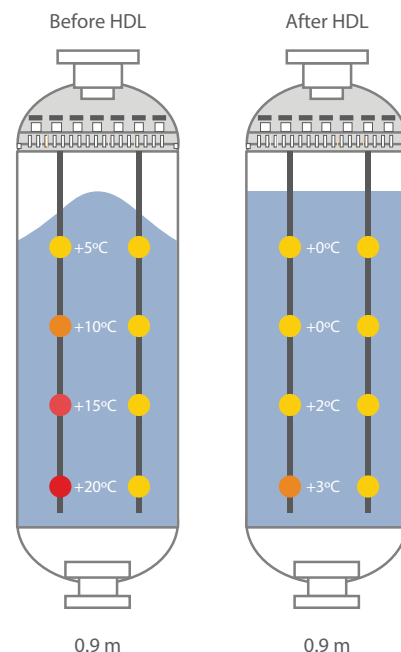
- **Improved density:** By using an optimal loading rate up to 30 m<sup>3</sup>/hr (1,050 ft<sup>3</sup>/hr), HDL can achieve bed densities up to 30% higher



**FIG. 7.** Catalyst loading rate (A) has an important influence on the average bed density achieved. Higher average density means that a great total mass of catalyst (B) can be loaded within the same reactor space.



**FIG. 8.** Example of EOR times for the three loading methods: sock loading, CDL and HDL.



**FIG. 9.** A reactor records severe temperature anomalies down its left side after sock loading or CDL (left). After reloading catalyst using HDL, temperature anomalies are almost eliminated (right).

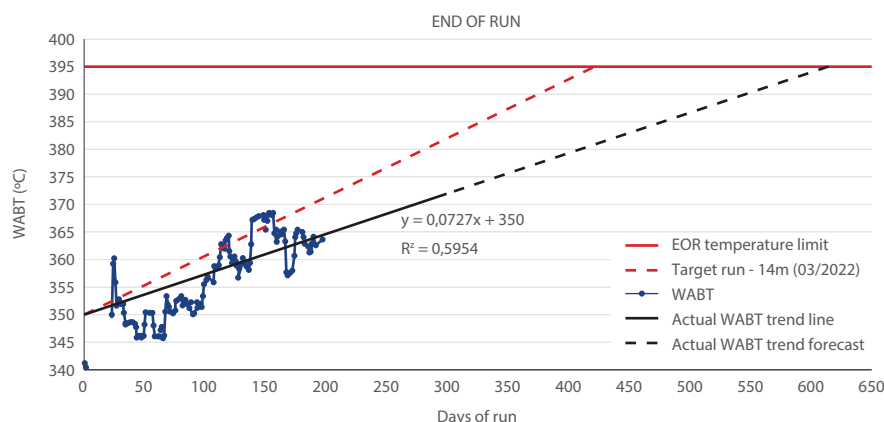


FIG. 10. Graph showing the evolution of WABT and extension of EOR time.

vs. sock loading and CDL, and can thus load as much as 30% more catalyst by weight (FIG. 7).

- **Increased homogeneity:** Optimal load rates enable catalyst particles to fall freely and separately across the full diameter of any reactor. In doing so, particles have time to settle in more stable, consistent and horizontal arrangements, resulting in more homogeneous loading density over the entire bed volume. This improves the liquid/gas distribution and lowers the risk of hotspot development within the catalyst bed. Additionally, HDL can load to within 30 cm of the overlying dispersion trays, thereby eliminating the need for top-up by sock loading. This reduces the risk of liquid/gas maldistribution and hotspot development.
- **Excellent catalyst integrity:** HDL uses low-friction materials and brushes at the mouths of the dispersion channels to minimize damage to catalyst particles, thereby eliminating nearly all dust and fine particles.

**Strategic benefits of HDL.** HDL provides multiple strategic benefits that make it the smart choice for operators looking to maximize unit and hardware performance, and ROI.

**Improved safety.** Safety should be the top priority for any operator. By eliminating the need for personnel to enter the reactor and by only requiring a single person to install and dismantle the machinery, HDL enables a much safer environment for catalyst handlers.

**Higher yields.** Enhanced liquid/gas flow distribution, optimized WHSV and improved vapor-liquid-catalyst interactions maximize product output per unit of run time.

**Lower TCO.** Although the initial price may be higher than alternative solutions, HDL can generate a healthy ROI by providing a cost-effective way to safeguard the performance of expensive catalyst and reactor internals, and to also reduce life-time maintenance costs.

**Longer run time and less downtime.** With no maldistribution, EOR temperatures are not reached prematurely, so the best use is made of the catalyst activity (FIG. 8). Additionally, the efficiency with which HDL machines can be loaded and dismantled can save as much as two shifts' worth of labor and time over the course of a cycle. Case Study 2 provides an example of how unit run time can be extended by using HDL.

**Reassurance.** Knowing that catalyst is well loaded means one less thing for the operator to worry about.

**How to minimize the risk of maldistribution.** To obtain the best performance out of expensive catalyst and state-of-the-art reactor internals, an increasing number of operators are unlocking major business value by embracing the long-term strategic benefits of high-quality HDL. To achieve this, reactor operators should:

- Be proactive in understanding the importance of catalyst loading in reactor performance—getting catalyst loading right at the start can save a lot of time, money and stress in the long term.
- Speak with experts on catalyst

loading and reactor internals to better understand how to maximize the performance of fixed-bed catalytic reactors.

- Think long term to ensure that short-term goals do not compromise the overall performance and success of the project.

### Case Study 1: Eliminating hotspots.

A process engineer for a mineral oil plant in Brazil reported that significant temperature anomalies (hotspots) had developed in a small, 0.9-m-diameter reactor. Using data from pairs of temperature sensors positioned inside the catalyst bed, the engineer calculated a temperature increase of as much as 20°C (68°F) from one side of the reactor to the other—a clear indication of maldistribution.

Deciding that the catalyst needed reloading, the engineer opted for the HDL method and technology. Following reloading, the temperature variation across the reactor was reduced to 3°C (37°F), which indicated that the maldistribution had been eliminated—a highly satisfactory result for the engineer (FIG. 9).

**Case Study 2: Extending run time.** A reactor operator at an oil refinery in the Czech Republic was planning to reload catalyst for two gasoil hydrotreater reactors of 2.8 m and 3.3 m diameters. Previously, loading was done using whip-based CDL; however, because of restrictive internal configurations, the quality of the loading was suboptimal.

The operator instead chose the HDL method and technology, and, after 7 mos, observed better performance in terms of reduced WABT. Based on new projections, the time to reach the EOR temperature of 395°C (743°F) was extended significantly beyond the initial 14-mos target (FIG. 10). **HP**

### NOTES

<sup>a</sup> Shell's high-dispersion (HD) tray

<sup>b</sup> CREALYST-Oil's CALYDENS® advanced catalyst loading system

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## Catalysts

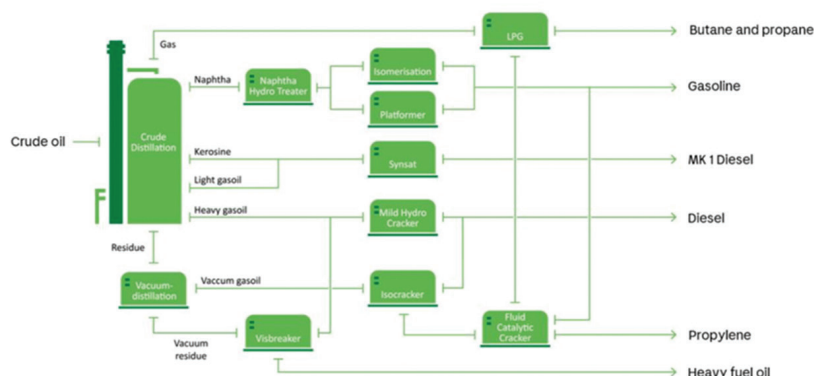
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## Partners maximize profitability during the pandemic

The COVID-19 pandemic can be viewed as one of the most challenging periods in the history of the oil and gas sector. Refineries worldwide faced difficult times operating at their turn-down capacities or even temporarily shut down units at the refinery. These unforeseen circumstances have put significant pressure on refinery volumes and margins to survive in this challenging market environment, forcing refiners to improvise. Unprecedented quarantines and lockdowns imposed due to COVID-19 had a serious effect on fuel demand and oil prices.

Since hydrocrackers are extremely flexible, they play a vital role in optimizing refinery economics. Hydrocrackers convert the bottom of the barrel, upgrading feedstocks into high-value fuels, lubricants and chemicals, which boost the value of refinery product slates. On top of adapting to cyclical market demands and the more stringent environment IMO regulations in 2020, refiners needed to act swiftly to remain competitive. The recent decline in demand forced refineries to run their hydrocrackers more economically by changing to new operational strategies to meet market demand.

**Preemraff Lysekil case study.** Preemraff Lysekil is a conversion refinery consisting of an atmospheric crude distillation unit (CDU), a vacuum crude distillation unit (VDU), a visbreaker unit (VBU), a mild hydrocracking unit (HCU), a fluid catalytic cracking unit (FCCU), a hydrodesulfurization unit (HDS), a catalytic reforming unit (CRU), an isocracking unit (ISO), and LPG units in addition to their hydrotreating units (**FIG. 1**).

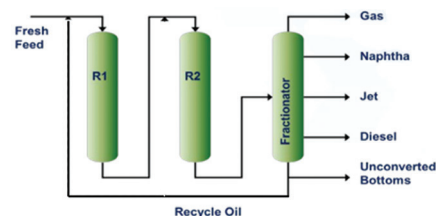


**FIG. 1.** Refining process at Preemraff Lysekil.

The product range varies from LPG to heavy fuel oil. One diesel product is called MK 1 Diesel, which is mainly applicable to the Swedish market, and has a specification on aromatics that must be < 5 vol%.

The Chevron Lummus Global (CLG)-designed Preemraff single-stage liquid recycle (SSREC) unit design (**FIG. 2**) and the ART-designed catalyst system enabled the Preemraff refinery to adapt to changing market conditions swiftly during the COVID-19 pandemic to maximize profitability while continuing to operate safely within design limitations. This article will discuss how that optimization of the SSREC hydrocracking operation gives refiners opportunities to improve performance in these dynamic circumstances. With CLG as the process licensor and ART as the technical service provider and catalyst vendor, the two companies' combined design and catalyst expertise created an opportunity to optimize the unit operation and maximize profitability.

The CLG-designed ISO unit<sup>a</sup> was designed in 2001 and built in 2004 to



**FIG. 2.** Simplified Preemraff ISO unit<sup>a</sup> SSREC configuration.

tackle the new environmental legislation in the EU, which set the maximum sulfur content in gasoline and diesel to 10 ppm. The unit was originally designed to process 385 m<sup>3</sup>/hr of a mixture of heavy atmospheric and vacuum gasoils in a once-through configuration with 50 vol% conversion to make a range of products, including full-range naphtha, kerosene, diesel and unconverted oil (UCO) for FCC feed. The unit design also included an integrated 165-m<sup>3</sup>/hr distillate unit<sup>b</sup> to make low aromatic content, full boiling range diesel. Unit turn-down was targeted to achieve operation at 60 vol% of the minimum design case



in each section. The unit operation was subsequently changed to a single-stage recycle mode using the existing lineups for startup circulation to improve middle distillate selectivity.

The UCO from the hydrocracker is used as feed to the FCCU. At first, the plan was to use a UCO flow corresponding to 50 vol% conversion of the maximum hydrocracker feed capacity. This amount of UCO proved to be challenging to process in the FCCU because of

the low coke production, so the demand for UCO dropped. This made it possible to use other catalysts in the hydrocracking unit and change the unit operation from single-stage once-through (SSOT) to SSREC to increase the conversion. By only changing the catalysts provided by ART, the unit increased conversion rates and no other investment was required.

Before the 2020 pandemic, the unit ran with high throughput at a typical conversion of about 63 vol%. During the

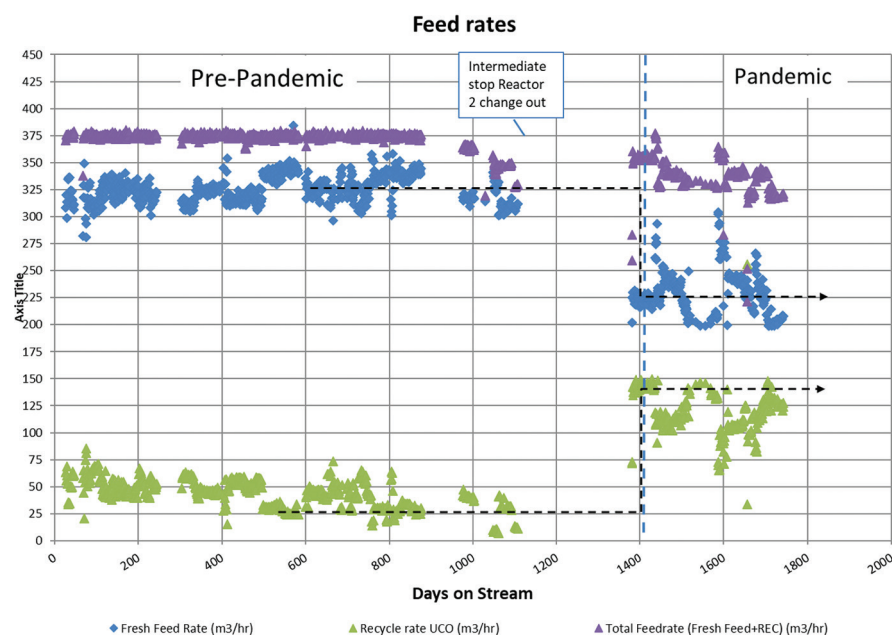
pandemic, demand for fuels dropped, so the unit was run at minimum throughput with about 85 vol% conversion to meet the contractual volumes of diesel. In this period, the FCCU was shut down due to economics. To reduce costs even further, there was a focus on minimizing the consumption of VGO. Together with ART, Preemraff optimized the operation so that conversion could stay continuously close to the 85 vol%–90 vol% range.

Another challenge during the last couple of years has been the new IMO legislation for sulfur content in bunker fuels that has required refineries to change the crude slate from high-sulfur crudes (mainly Urals) to mainly low-sulfur crudes (Johan Sverdrup, Gullfaks and Oseberg). For the hydrocracker, this meant a reduction in sulfur content in the VGO from about 1.5 wt% to 0.5 wt% S, which was made possible through close cooperation between ART/CLG technical services and Preemraff operations.

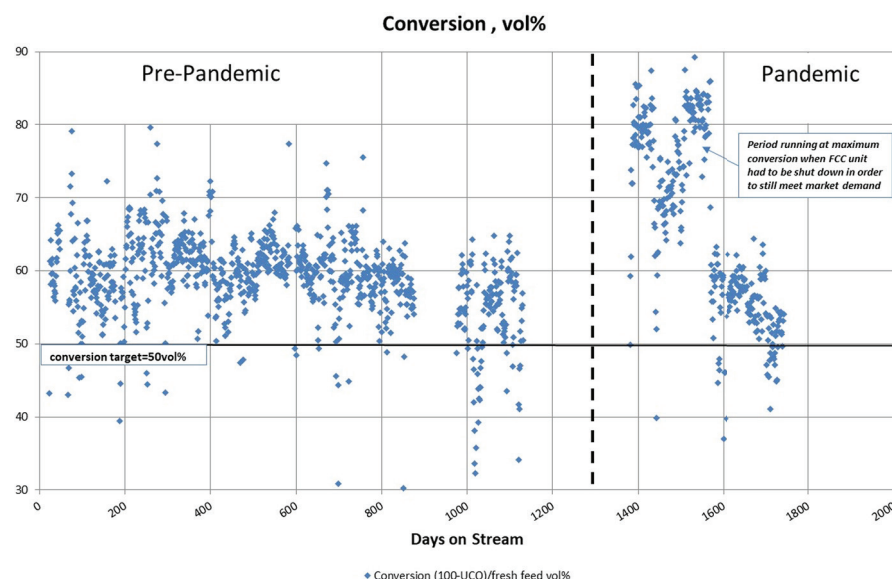
**An improved catalyst system for Preemraff.** Starting from the cogel-based catalysts<sup>a</sup> in the 1960s, scientists at Chevron's Richmond Technology Center (RTC), its global headquarters for innovation, have developed and continue to expand the family of catalysts<sup>a</sup>. This effort has been in response to the changing demand of refiners—including Chevron—to be able to process more difficult feeds, produce more and better quality desired liquid products, operate longer on each charge of catalysts, and deliver superior heavy polynuclear aromatics (HPNAs) management by chemical means.

Chevron scientists have utilized varying hydrogenation metals (from base metal to noble metals), and a combination of amorphous silica-alumina (ASA) and crystalline silica-alumina (i.e. zeolites) to customize the catalysts<sup>a</sup> for each application.<sup>1–4</sup>

Optimization of the hydrocracking unit catalyst system, cycle-over-cycle, helped Preemraff increase flexibility further during the pandemic and maximize conversion. The previous cycle showed a surplus of activity to increase the mid-distillate yield cycle-over-cycle. As a result, a more selective system was designed for the current cycle, which enabled the client to use the extra flexibility to increase conversion further without jeopardizing the yields during the pandemic.



**FIG. 3.** Mode of operation pre-pandemic and pandemic period limiting fresh feed intake to the bare minimum during the COVID-19 pandemic.



**FIG. 4.** Hydrocracking conversion levels, pandemic and pre-pandemic.

The luxury of the versatile and flexible SSREC design and the catalyst system enabled Preemraff to run economically during the pandemic, allowing them to continue running by adjusting feedrates to meet decreased market demand. Additionally, leveraging the catalyst system design, Preemraff operations worked with the author's company to fine-tune operations to maximize conversion and reduce fresh feedrate due to changing market demand. Close cooperation between ART/CLG technical services and the Preemraff operations team was crucial to operate safely within design limitations and transfer to the new mode of operation.

The transitions to different modes of operation are shown in FIGS. 3 and 4 (note the significant changes in recycle and fresh feed intake).

**Prior to and during the pandemic.** Pre-pandemic (prior to 2020), Preemraff focused on maximizing fresh feed intake and conversion while minimizing recycle, achieving maximum mid-distillate yields and securing the minimum UCO amount (130 m<sup>3</sup>/hr) to feed the FCCU. After 2020, minimizing fresh feed intake and maximizing conversion by maximizing unconverted oil recycle simultaneously was required to achieve maximum mid-distillate yields. Proper heat management was required to maintain sufficient heat in the first and second reactors to keep conversion going during the transition while changing modes of operation stayed within design limitations.

Another challenge the client faced was running low-sulfur North Sea crudes while maintaining sufficient heat in both reactors to ensure ongoing conversion. The challenge was to reduce fresh feed intake while running these low-sulfur North Sea crudes and simultaneously increasing unconverted oil recycle, which significantly affects the heat of reaction in the different beds in the first and second reactors. Consequently, heat management of the whole unit has changed significantly, running in this new mode of operation (e.g., running low-sulfur North Sea crudes). While reducing feed-

rate, special care was taken to keep conversion going until minimum design requirements were met, running all equipment downstream.

**The SSREC design, combined with the designed catalyst system, has shown to be highly flexible to adapt to continuously changing market circumstances by allowing the unit to be run in different modes of operation at low and high conversion levels for the two cycles.**

During and after the COVID-19 pandemic (FIG. 4), the refinery minimized fresh feed intake and maximized recycle conversion to achieve maximum mid-distillate yields, running much more profitably. During this period, the FCCU was shut down due to economic reasons, so no UCO feed was required to feed the FCCU. Beginning in 2021, the FCCU was started up again and a minimal UCO amount was required to meet the FCCU requirements running at low capacity. Surplus activity in the 2016–2019 cycle resulted in further improvement to a more mid-distillate selective catalyst system.

In FIG. 5, four distinct segmented periods are selected to demonstrate the operational requirements through the pandemic.

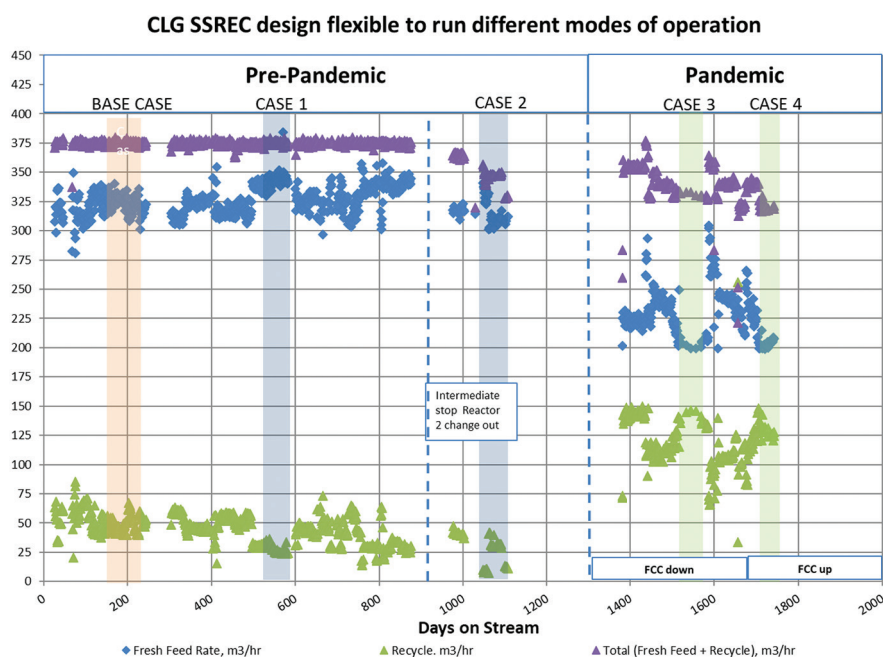
#### Pre-pandemic (2016–2019):

1. 2018: Conversion increased to utilize surplus activity left until end of the run

2. 2019: Reactor 2 catalyst system with a more mid-distillate selective system during an intermediate shutdown

#### Pandemic (2020-onwards):

3. 2020–2021: FCCU shut down during pandemic
  - a. Opportunity to run the hydrocracker at maximum conversion running at a bare minimum fresh feed intake to continue to meet contractual obligations
  - b. Opportunity to convert maximum UCO required as no UCO was required to feed FCCU
  - c. Opportunity running different



**FIG. 5.** Four distinct modes of operation visualized vs. the Base Case (filtered data selected).

low-sulfur crude slate during the pandemic to meet IMO bunker fuel specifications

4. 2021-present: FCCU online again; minimum UCO amount required to feed the FCCU.

These four distinct modes of operation selected (segmented data) vs.

a Base Case are visualized in **FIGS. 6 and 7**: ~320/65 m<sup>3</sup>/hr (fresh feedrate/UCO recycle rate, hereafter). Minimum UCO-flow requirement to the FCCU = 130 m<sup>3</sup>/hr.

**Pre-pandemic:** Base Case: ~320/65 m<sup>3</sup>/hr; fresh feedrate at 320 m<sup>3</sup>/hr and UCO recycle rate at 65 m<sup>3</sup>/hr re-

cycle; UCO flow requirement to FCCU at 130 m<sup>3</sup>/hr.

- Case 1: ~350/25 m<sup>3</sup>/hr; to maximize fresh feed intake with the same UCO flow to the FCCU (i.e., 130 m<sup>3</sup>/hr)
- Case 2: ~325/35 m<sup>3</sup>/hr; Reactor 2 replaced with a more mid-distillate selective catalyst with the same UCO flow to the FCCU (i.e., 130 m<sup>3</sup>/hr)

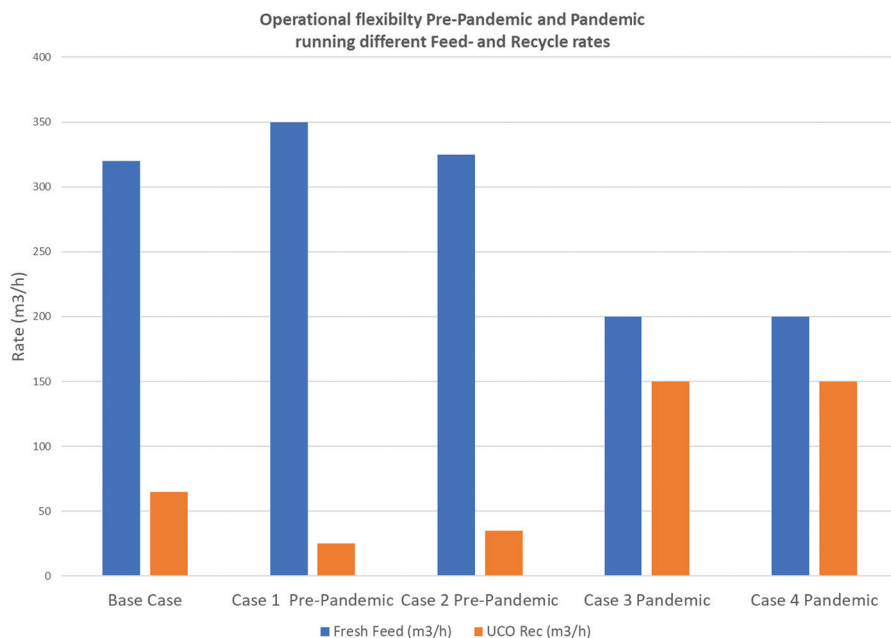
#### Pandemic:

- Case 3: ~200/150 m<sup>3</sup>/hr; FCCU down, maximize hydrocracking conversion as UCO required to feed the FCC is not needed
- Case 4: 200/150 m<sup>3</sup>/hr; FCCU online with reduced UCO flow to the FCCU at ~85 m<sup>3</sup>/hr.

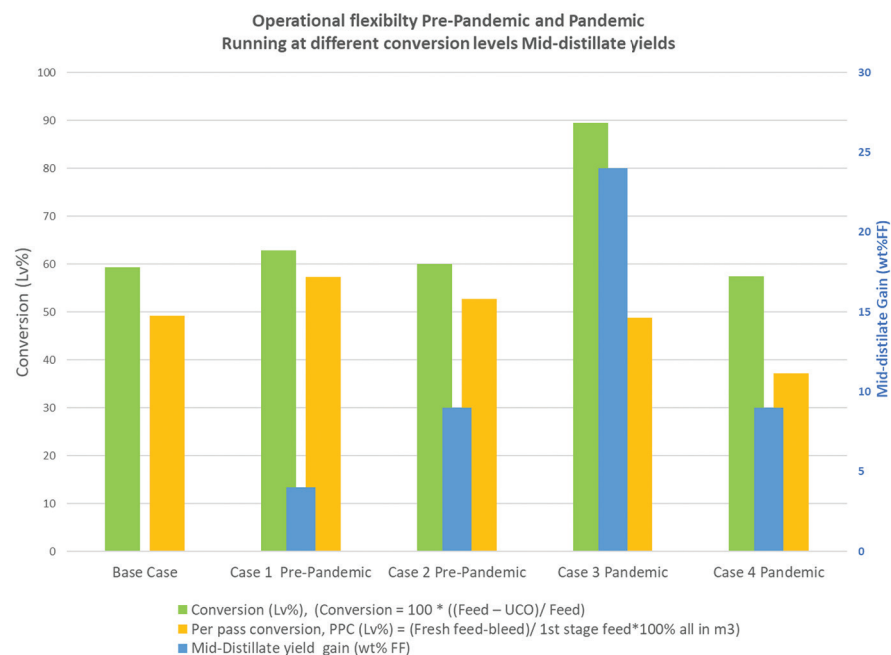
The pre-pandemic mode of operation maximized conversion by increasing fresh feed intake while still meeting the minimal UCO feed requirement. Pre-pandemic, ART helped Preemraff to replace a second-reactor catalyst earlier than the planned turnaround. The company advised the client to optimize the temperature profile to make optimal use of the more selective catalyst system in Reactor 2, achieving additional mid-distillate gain of > 4 wt% on a fresh feed basis.

During the pandemic, the FCCU was temporarily shut down. The mode of operation was to reduce fresh feed intake to the minimum while maximizing conversion and still meeting client obligations. During the most recent cycle, which occurred during the pandemic, performance improved further by increasing conversion, enabling the unit to increase middle-distillate output by reducing fresh feed intake and running low-sulfur North Sea crudes. **FIG. 7** shows that Case 3 runs at the highest conversion around 90 vol% with a mid-distillate gain of > 27 wt% on a fresh feed basis vs. the Base Case when the FCCU was down. Case 4 shows a mid-distillate gain of ~9 wt% on a fresh feed basis at a reduced conversion level of 58 vol% when the FCCU was up again, meeting the minimum UCO requirement to feed the FCCU.

**Operational challenges during the pandemic.** During the transition between the different modes of operation, proper heat management is required to always keep sufficient heat in both the first and second reactors to meet the



**FIG. 6.** Operational modes of four distinct cases running at different fresh feed and recycle rates at different hydrocracking conversion levels vs. a Base Case.



**FIG. 7.** Operational modes of four distinct cases running at different hydrocracking conversion levels and mid-distillate gain vs. a Base Case.



desired conversion. Reducing fresh feed intake and increasing UCO recycling reduced the heat of reaction in the first reactor. Additionally, simultaneously changing to low-sulfur North Sea crudes further reduced the heat generation. A smooth transfer between the different modes of operation requires an in-depth understanding of the SSREC CLG design and ART catalysts system to transfer smoothly between the different modes of operation and respond to the reduced market demand.

Besides changes in the inlet temperature of Reactor 1 posted by reduced fresh feed and high UCO recycling, high conversion leads to the risk of HPNA accumulation and undesired secondary cracking. Only catalysts with excellent hydrogenation activity can meet this type of challenge. One of the key features of the proprietary catalysts<sup>a</sup> is the uniformly dispersed cracking and hydrogenation metals components. The linear relationship of middle distillate yield vs. hydrocracking conversion in **FIG. 8** is another piece of evidence. No signs of overcracking and HPNA accumulation are observed in the conversion range from 50% to > 90%.

**Takeaway.** CLG's SSREC design in combination with ART's designed catalyst system has shown to be extremely flexible to adapt to continuously changing market

circumstances by allowing the unit to be run in different modes of operation over the two cycles. Pre-pandemic, Preemraff maximized fresh feed intake, running high conversion mode while maximizing mid-distillate yield. During the pandemic, Preemraff minimized fresh feed intake to the minimum. The company ran at the highest conversion to convert maximum UCO into mid-distillates while running spot market low-sulfur North Sea crudes. Using the SSREC design combined with the catalyst system while running the low-sulfur North Sea crudes, Preemraff met the IMO bunker fuel specifications to run most profitably during the pandemic.

During the transition between the different modes of operations, the more mid-distillate selective catalyst system showed no sign of HPNA accumulation while increasing conversion level. The key to a successful change in the mode of operation was continuous two-way communication and collaboration between Preemraff's operational team and the authors' companies' technical service. Unit design flexibility and access to the companies' technical services enabled Preemraff to optimize unit performance within design limits and ensure the unit always runs safely within design limits. **HP**

#### ACKNOWLEDGEMENT

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#### NOTES

- <sup>a</sup> Chevron Lummus Global's ISOCRACKING®  
<sup>b</sup> Chevron Lummus Global's ISOFINISHING®

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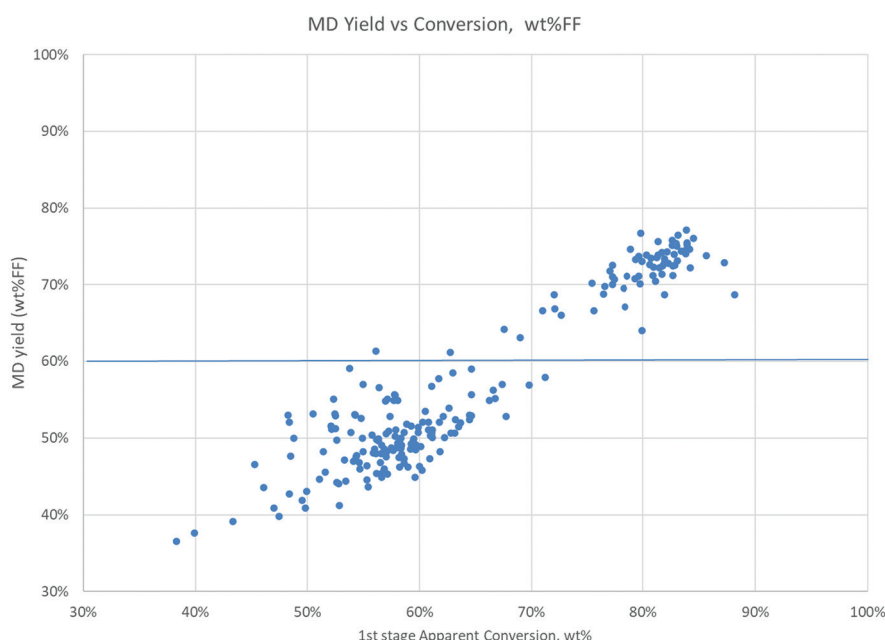
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**FIG. 8.** Summary of middle distillate selectivity vs. conversion on fresh feed of all cases.

## Catalysts

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## Flexibility in catalyst technology for improved bottoms upgrading

Bottoms product from fluidized catalytic cracking (FCC) is typically one of the least valuable products from a refinery. As a result, strong bottoms cracking in the FCC process is needed by refiners. While maximization of bottoms upgrading might be desired, FCC feed, unit constraints, operation decisions and catalyst selection all determine the ability of an FCC unit (FCCU) to upgrade bottoms into more valuable products. Due to the wide variability in these factors, there is not a one-size-fits-all catalyst solution to improve bottoms upgrading in every FCCU. This work details three separate case studies of back-to-back catalyst trials in FCCUs around the world. In each case, the specific characteristics of the FCCU were considered to select a catalyst technology that improved bottoms upgrading.

The first study describes how a catalyst technology and zeolite-to-matrix surface area (Z/M) were optimized to improve bottoms destruction in a North American FCCU. In this case, the lowest Z/M option was not optimal, and a more moderate Z/M provided the best upgrading route for the FCCU. In contrast, the second case study details how a low Z/M catalyst provided the best bottoms upgrading in a European FCCU. The third case study occurred at a heavy resid unit in Asia. The bottoms upgrading optimization was realized using a high Z/M catalyst that improved coke selectivity. From these three cases, it can clearly be seen that the optimum FCC catalyst for upgrading bottoms will vary depending on the FCCU's specific requirements, operations and constraints.

**Case Study 1.** The first example is from a North American FCCU. This example

shows that changing catalyst technology and tuning Z/M to an optimum level can result in improved bottoms upgrading in an FCCU. This FCCU processed vacuum gasoil with mild-to-moderate metals levels and used BASF Catalyst A, a high Z/M [equilibrium catalyst (Ecat) Z/M = 2] proprietary catalyst<sup>a</sup> to achieve high conversion. The objectives of the FCCU shifted to incentivize further bottoms destruction. As a result, two new catalysts were trialed in the FCCU to meet the objective of improving bottoms upgrading without sacrificing conversion. One catalyst was not from the authors' company and contained a much lower Z/M level (Ecat Z/M = 0.8) vs. Catalyst A. The new catalyst aimed to use higher matrix content to achieve bottoms destruction. The authors' company proposed a different FCC catalyst<sup>b</sup> (Catalyst B) with a more moderate Z/M (Ecat Z/M = 1.4). The new BASF FCC Catalyst B<sup>b</sup> uses the authors' company's improved zeolite-Y technology and was chosen due to its superior mesoporosity, which allows for better bottoms upgrading without sacrificing conversion to liquid products.

**TABLE 1** provides a summary of key yields at constant conversion during the trials. There are several notable outcomes. First, BASF Catalyst B resulted in lower bottoms and higher light cycle oil (LCO) yields than either of the other two catalysts, despite experiencing elevated contaminant metals levels during the trial. The LPG + gasoline yields also increased vs. the other catalysts. Similarly, the dry gas yield was lower than the other catalysts despite having > 500 ppm more contaminant metals on the Ecat—an indication of more selective cracking.

However, examining the yield shifts at constant conversion only told part of the story, as a key goal of the new BASF Catalyst B was to improve bottoms upgrading without sacrificing conversion. **FIG. 1** shows the bottoms vs. conversion and LCO vs. conversion results from the trial of the three different catalysts. The low Z/M, non-BASF catalyst had lower activity than the incumbent BASF Catalyst A, and this can be seen in the consistently lower conversion levels. Any potential benefit of improved or increased matrix amount could not be

**TABLE 1.** Summary of yields from each trial period

	Incumbent Catalyst A <sup>a</sup>	Non-BASF catalyst	New Catalyst B <sup>b</sup>
Ecat Z/M	2	0.8	1.4
Ecat, nickel (Ni) + vanadium (V)	3,617	3,645	4,185
Conversion	73.5	73.5	73.5
Dry gas	2.8	3	2.9
Gasoline + LPG	66.7	66.1	66.3
LCO	16.8	16.7	17.2
BOT	9.7	9.8	9.3

realized due to the loss in conversion. As a result, there was no improvement in bottoms upgrading compared to the incumbent Catalyst A.

The benefit of both the improved zeolite-Y technology and the more moderate Z/M level Catalyst B can be seen in **FIG. 1**. The FCC proprietary catalyst<sup>b</sup> imparted more activity than the low-Z/M, other catalyst, resulting in higher conver-

sion levels. While the conversion levels were lower than the incumbent Catalyst A, the impact of the improved porosity and matrix technology are seen as the bottoms upgrading noticeably improved vs. the other two catalysts—shown by the higher LCO and lower bottoms yields. This trial provides an example where the catalyst technology must be balanced with optimization of other cat-

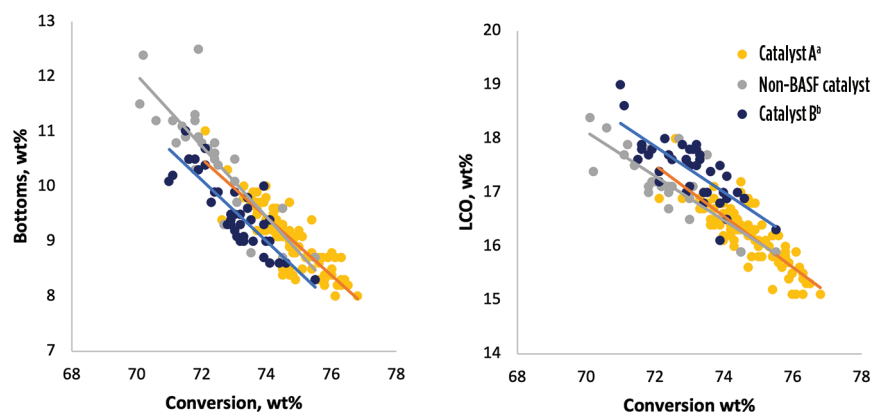
alyst parameters (in this case, Z/M) to achieve bottoms upgrading goals.

**Case Study 2.** This case study involved a European refinery whose main objectives were to improve coke selectivity and minimize bottoms product and dry gas yields. The incumbent catalyst<sup>c</sup> (Catalyst C) was a moderate-to-low Z/M catalyst designed to minimize bottoms and maximize fuels without increasing dry gas and coke. It is a precursor to the authors' company's newer, enhanced Catalyst D<sup>d</sup>, which improves upon the incumbent catalyst to meet the same objectives. The refinery commissioned a catalyst evaluation and tested various catalysts. A non-BASF catalyst showed very favorable testing outcomes, promising lower bottoms yields among other benefits. The refinery decided to change from the incumbent Catalyst C and trial the other catalyst in the FCCU.

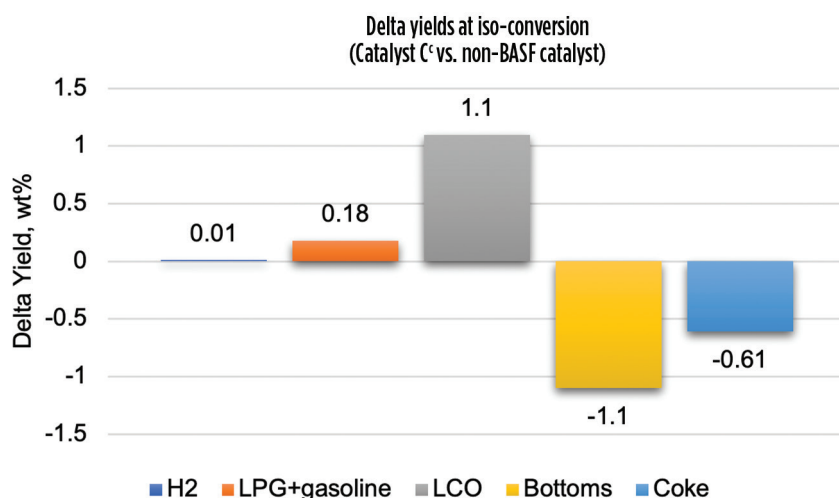
After a few months of the industrial trial, the refinery—after having tracked the chemical markers and the catalyst turnover—decided that the performance seen in the unit was not in alignment with expectations based on testing. Furthermore, the regenerator temperature was higher due to delta coke, the wet gas compressor was constrained due to an increase in dry gas and slurry yields were noticeably higher. The refinery decided to change back to BASF Catalyst C and perform a post audit to determine the industrial yield shifts.

Ecat samples from the non-BASF catalyst's trial period and Catalyst C's periods were chosen for post-audit analysis. The ECAT metals levels between the two time periods were comparable (both samples had > 4,500 ppm Ni + V), but nearly twice as much ZSM-5 was used during Catalyst C's period; therefore, the analysis was done on LPG + gasoline to eliminate additive effects on selectivity.

The post-audit results are shown in **FIG. 2**. These results reveal large differences in bottoms upgrading and overall liquid yields between the two catalyst trials. The non-BASF catalyst resulted in lower LPG + gasoline and LCO yields. Furthermore, the LCO/bottoms ratio was worse with the other catalyst, going from 1.3 wt%/wt to 1.1 wt%/wt. These changes were not captured in pre-trial testing, went against



**FIG. 1.** Bottoms upgrading vs. conversion in Case Study 1's trials at a North American FCCU.



**FIG. 2.** Post-audit yield results from Case Study 2.

**TABLE 2.** Yield selectivities at iso-coke (8.5 wt%)

Yield, wt%	Non-BASF catalyst	Catalyst E <sup>e</sup>
Hydrogen	0.61	0.56
Dry gas	3.2	3.3
Total LPG	20.4	21.1
Gasoline	39.1	41.3
LCO	15.6	14.7
Bottoms	13.3	11
Conversion	71.2	74.3
LCO/BOT	1.2	1.3



unit objectives and were detrimental to unit profitability.

**Case Study 3.** The final case study of tailoring catalyst technology and design to meet the bottoms upgrading objectives of an FCCU was at an Asian refinery. The refinery wanted to increase FCC profitability by improving bottoms upgrading, while maintaining high conversion and coke selectivity despite sporadic metals poisoning episodes and maintaining Ecat metals levels greater than 7,500 ppm of Ni + V. The unit was often limited in bottoms upgrading ability due to reaching regenerator temperature limits.

Using an activity model fine-tuned to the FCCU's operation, a catalyst was proposed (BASF Catalyst E<sup>a</sup>) to maximize conversion in a heavy resid environment. The objective for this catalyst was to offer improvements to the incumbent catalyst through enhanced pore architecture and metals passivation. Catalyst E was evaluated—along with other candidates—through pilot plant testing, modeling and sensitivity studies and was eventually selected for trial.

**TABLE 2** details the post-audit results using both catalysts at iso-coke conditions. BASF Catalyst E demonstrated improved coke selectivity by showing significantly higher conversion at iso-coke levels. As a result, LPG and gasoline yields were also higher. Additionally, the hydrogen yield of Catalyst E was lower despite the higher conversion, a result of the strong metals passivation of the catalyst. Finally, LCO/BOT and overall bottoms yield were both improved, demonstrating that this catalyst was the right fit for optimizing bottoms upgrading in this unit.

**FIG. 3** shows two cross plots from the post-audit study of this catalyst trial. The strong coke selectivity and improved bottoms upgrading provided by Catalyst E can further be seen in this analysis. Catalyst E demonstrated slightly higher conversion yet consistently lower coke make. Similarly, Catalyst E was also able to crack significantly more bottoms at comparable coke levels. Once again, despite being a different technology than the catalysts seen in the previous two trials, consideration of the specific requirements of this unit led to an improvement in bottoms upgrading through catalyst selection.

**Takeaway.** As one of the least valuable FCC products, the need to minimize bottoms is expected to increase as pressure on refiners to get the most out of every barrel of feed intensifies. The three trials detailed in this article illustrate that understanding the needs and constraints of each unit is critical to maximizing bottoms upgrading through FCC catalyst selection, as the strategy for the appropriate catalyst technology used in each trial is different. Three different catalysts were used across the three trials. Despite the

three catalysts being different, bottoms upgrading was improved significantly in each case because close collaboration between the refinery and the FCC catalyst supplier ensured that the catalyst provided met the precise needs of the unit and delivered maximum profitability. **HP**

#### NOTES

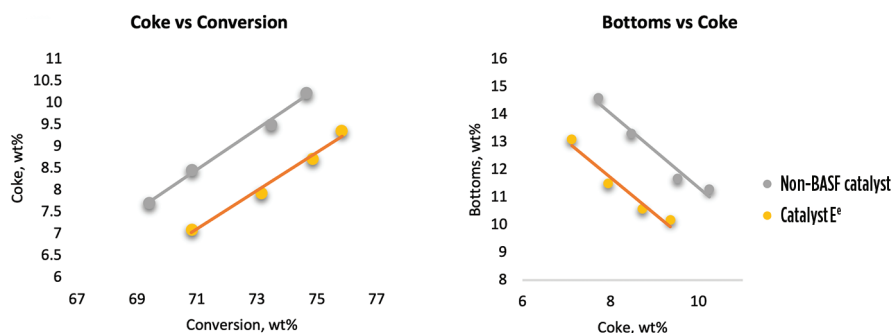
<sup>a</sup> BASF's NaphthaMax<sup>®</sup> catalyst

<sup>b</sup> BASF's Luminate<sup>®</sup> catalyst

<sup>c</sup> BASF's Aegis<sup>®</sup> catalyst

<sup>d</sup> BASF's Altrium<sup>®</sup> catalyst

<sup>e</sup> BASF's Fortress<sup>®</sup> NXT catalyst



**FIG. 3.** Selected yield plots from Case Study 3's post-audit study.

## Development/industrial application of FCC catalyst for boosting high-octane gasoline production

Globally, crude oil is trending toward being heavier; the proportion of heavy crude oil reserve is expected to be 50% of the entire recoverable oil reserve moving forward from 2020 (FIG. 1). The global oil refining business is facing extreme pressures not only due to the heavier and inferior raw materials, but also from the mounting demands for environmentally friendly refining processes and light, clean petrochemical products. This makes the transformation of heavy oil the key factor in the productivity and economic benefits of refineries.

The pro-hydrogenation of raw materials for catalytic cracking is one of the most well-known techniques to increase operating efficiency and ameliorate the quality of both raw materials and petrochemical products. Nevertheless, the proportion of polycyclic naphthenes and naphthenic aromatics could be enhanced dramatically (e.g., the amount of cyclic naphthenes could account for more than 50%). Moreover, it is well-known that both the increase in heavy oil and the increase of boiling range of distilled oil cause a pronounced growth of the ratio of polycyclic naphthenes and naphthenic aromatics in the raw materials.

For these reasons, one of the most consequential problems in refining techniques is how to make the efficient and rational transformation of polycyclic naphthenes—including the control of the hydrogen transfer (HT) reaction and the promotion of the ring-opening reaction—so that more valuable light petrochemical products can be obtained.

Unfortunately, conventional fluid catalytic cracking (FCC) catalysts show great potential in the HT reaction, yet their abilities in the ring-opening reaction are still relatively low. This accounts for low yield, low octane number of gasolines and the elevation of coke. Therefore, it is imperative to find a strategy to optimize the distribution of catalytic cracking production and enhance the octane number of gasolines.

This article details a new FCC catalyst to concurrently increase the yield of gasoline and decrease the formation of coke. Based on the perceptions of a reaction mechanism, the study also discusses how the designs of the new catalyst developed to meet the aforementioned requirements. Additionally, an industrial application case is introduced.

**Strategic design of an efficient catalyst.** The most prevalent FCC catalyst is usually comprised of two major components (zeolite and matrix), which lead to two different routes to improve the efficiency of the FCC catalyst: one is to create new zeolite materials, the other is to develop a new matrix.

One of the most widely used zeolite materials in FCC is Y zeolite due to its unique pore structure, high stability and proper acidity. However, the size of polycyclic naphthene molecules is slightly larger than the pore window size of Y zeolite, which impedes the diffusion of those molecules into the pores, thus promoting the secondary reaction. The authors propose that the rational way to augment its efficiency is to create Y zeolite with a small crystal size. Compared to the large-sized Y zeolite, the smaller has a much larger external specific surface area, which increases active sites on the external surface, thus improving the catalytic cracking conversion of heavy oil or residue. Meanwhile, smaller Y zeolite has a better dispersion of acid centers, which accordingly boosts the availability of acid centers. Moreover, the reduction of the crystal size truncates the channel, decreasing the odds of collision between different molecules, which diminishes the yield of cokes caused by the bimolecular reaction (FIG. 2).

Notwithstanding, the hydrothermal stability of the Y zeolite could be marred by decreasing its crystal size. Accordingly, for the development and application of zeolite with small crystal size, it is crucial to improve its hydrothermal stability. With rigorous experiments and theoretical guidance, the authors' company managed to create a new type of Y zeolite. The size of this new Y zeolite is only ~500 nm, which is about half of the regular NaY. As shown in FIGS. 3A–3D, the stability of the new Y zeolite (marked

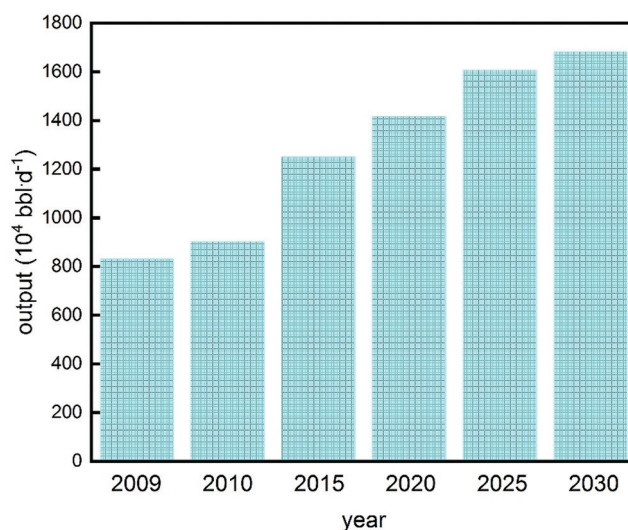


FIG. 1. The increasing trend of heavy oil from 2009–2030.

as SCY) is much stronger than the commercial small-sized Y zeolite while similar to the regular NaY zeolite. It is well-known that the synthesized zeolite materials entail a strong resistance to the steam during the application in a real refinery. Normally, the structure of regular zeolite can be dramatically destroyed by the steam at high temperature. To enhance the hydrothermal stability of the authors' company's SCY zeolite materials, a gas-phase hyperstabilization method was conducted. As shown in FIG. 3D, although the relative crystallinity of the SCY zeolite is almost identical to the commercial NaY zeolite, the crystallinity retention of SCY is significantly higher than its counterpart.

**Strategy for the new matrix.** In addition to zeolites, matrix should also be considered as another important component in terms of alteration of catalyst activity. The poor accessibility of heavy oil molecules to the active centers of zeolites significantly impedes their diffusion in the zeolite channels. Therefore, the pre-activation of heavy oil molecules on a specific matrix is im-

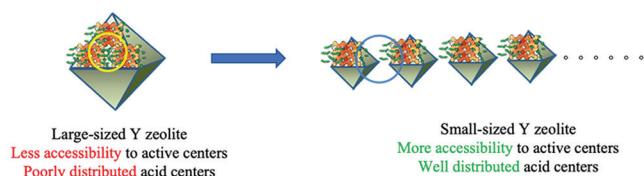


FIG. 2. Simplified explanation of difference between different-sized zeolite materials.

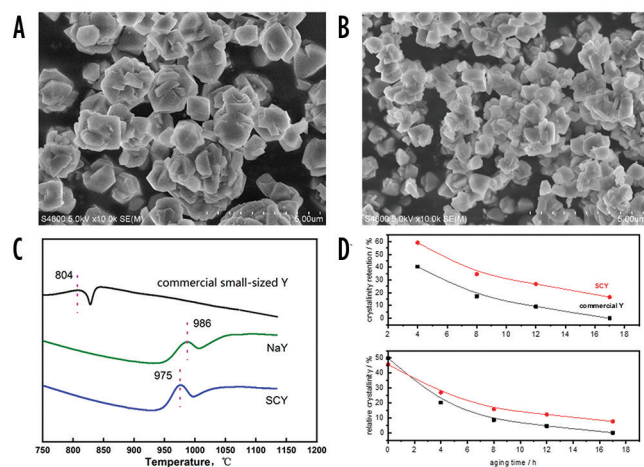


FIG. 3. TEM image of (A) commercial NaY zeolite, (B) SCY zeolite, (C) crystalline structure collapse temperature of different Y zeolites and (D) relative crystallinity and crystallinity retention of SCY and NaY.

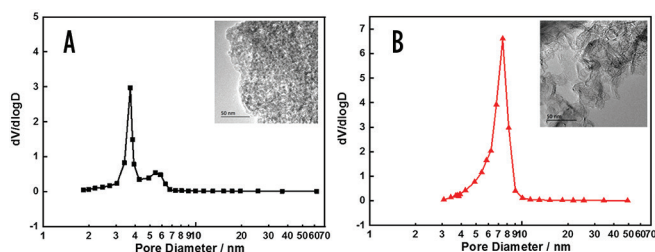


FIG. 4. Pore size distribution curve of (A) commercial  $\text{Al}_2\text{O}_3$  and (B) LOM. Insets are the TEM images of commercial  $\text{Al}_2\text{O}_3$  and LOM.

perative, requiring the development of a new matrix with proper size. One of the underlying challenges is to balance the matrix's pre-activated ability and the selectivity of coke formation. Therefore, to curb the formation of coke, the Lewis acid in the matrix must be further reduced and weakened. Compared to a regular matrix, the newly developed matrix, marked as LOM, shows a unique fabric-like morphology with 8-nm mesopores, which is higher than the pore diameter of the regular matrix (FIG. 4). The larger pore diameter is not only beneficial to the diffusion of large molecules, but decreases the possibility of bimolecular reaction and (consequently) the yield of coke. Further experiments confirm that the amount of whole Lewis acid as well as the amount of strong Lewis acid in the novel matrix decreases dramatically, contributing to less coke formation (TABLE 1).

**Industrial application of the new catalyst<sup>a</sup>.** Based on the aforementioned experimental studies, the new catalyst<sup>a</sup>, combined with SCY zeolite and LOM matrix, was successfully produced. It should be highlighted that this catalyst was used in an industrial FCCU from September 15, 2019, to improve the conversion and product distribution of heavy oil and boost the economic performance. The FCCU mentioned is owned by

TABLE 1. Acidity of Lewis acid of different matrix

	Acidity of Lewis acid/ ( $\mu\text{mol/g}$ )	
	Total Lewis acid	Strong Lewis acid
$\text{Al}_2\text{O}_3$	31.2	18.9
LOM	17.8	3.3

TABLE 2. Primary properties of raw materials used in blank calibration and summary calibration

	Blank calibration	Summary calibration
Density, $\text{kg/m}^3$	921.8	926.5
Carbon residue, %	2	2.96
Basic nitrogen, $\mu\text{g/g}$	785	737
Saturated hydrocarbons, %	57.3	58.8
Aromatic hydrocarbons, %	28	27
Gums, %	14.3	13.7
Asphalts, %	0.4	0.5

TABLE 3. Basic operation conditions in blank calibration and summary calibration

	Blank calibration	Summary calibration
Inlet rate, $\text{t} \times \text{h}^{-1}$	112.7	115.3
Residue ratio, %	64.5	66.9
Pre-heated temperature, $^{\circ}\text{C}$	200	201
Reaction temperature, $^{\circ}\text{C}$	515	515
Reaction pressure, kPa	205	213
Regeneration pressure, kPa	232	236
Main flow, $\text{m}^3 \times \text{min}^{-1}$	1,935	1,842
Dense bed temperature in regenerator, $^{\circ}\text{C}$	715	715
Lean bed temperature in regenerator, $^{\circ}\text{C}$	678	681

Qilu Petrochemical Co. and the authors' company, and its designed processing capability is ~800,000 tpy of crude oils. The high and low side-by-side towers are adopted as the reaction-regeneration system. The amount of catalyst added per day is around 2.5 t, which is equivalent to the former catalyst. Considering the standard conditions of changing catalyst and the common cause of catalyst loss, the storage of the new catalyst<sup>a</sup> in the unit reached 100% by March 9, 2021. The catalyst change was performed steadily without any aberrant loss of catalyst. Two representative times were chosen to reflect the potential of the new catalyst. The summary calibration (marked as SC) was conducted from March 9 to March 10, 2021, using the new catalyst, and the blank calibration (marked as BC) was from September 11 to September 13, 2019, when the previous catalyst<sup>b</sup> was used in the same refinery.

**Properties of raw oil.** The properties of raw materials exert notable influence on catalytic performance, so it is imperative to bring up the properties of raw materials during the calibration. The properties of raw materials during BC and SC are shown in **TABLE 2**. While the properties from both calibrations are similar, some disparities exist. The carbon residue in SC is ~2.96%, which is 0.96% higher than that in BC. It is supposed that the higher amount of carbon residue would cause an increased formation of coke. Therefore, compared to the raw materials used in BC, those used in SC have an adverse effect on the catalytic activity of the new catalyst<sup>c</sup>.

**Basic operating conditions.** The basic operating conditions during blank calibration and summary calibration are shown in **TABLE 3**. Some negligible changes exist between the two calibrations. It should also be noted that the residue ratios in both calibrations are high.

**Properties of equilibrium catalyst (E-Cat).** The E-Cat's properties are shown in **TABLE 4**, including the specific surface

area, the microporous specific surface area, the total pore volume and the volume of micropores. The calibration is discernibly higher than the one used in the blank calibration. The larger specific surface area and pore size are conducive to the interaction between the organic molecules and acid centers on the catalyst and the diffusion of big molecules in catalyst channels, improving the conversion of heavy oil. These results indicate that the new catalyst<sup>a</sup> achieved the designed goal with a greater ability for the conversion of heavy oil. It should be also noted that a stable operation of the unit and a normal fluidization of the catalyst were presented, which means the authors' company's catalyst could meet the operating criteria.

**Distribution of FCC products and their properties.** To present the potential of the new catalyst, the conversion, selectivity, product distribution and properties are provided, as well. As shown in **TABLE 5**, with the same operating conditions, the yield of gasoline in the summary calibration is 45.9% (1.03% higher than the one in blank calibration) while the yield of coke is reduced by 0.3%—the yield of liquid products was also increased by 1.87%. According to the processing capability and the average prices of the raw materials and products, the cost of the raw materials could be reduced by more than \$2 MM/yr while the profit increment from the gasoline could reach \$1.8 MM/yr.

Meanwhile, the reduction in coke formation also results in a decrease of CO<sub>2</sub> emissions of ~10,000 tpy. The new catalyst does ameliorate the transformation of raw materials and the dis-

**TABLE 4.** Primary properties of E-Cat in blank calibration and summary calibration

	Blank calibration	Summary calibration
<b>Physical property</b>		
Specific surface area, m <sup>2</sup> × g <sup>-1</sup>	112.7	133
Specific surface area of micropore, m <sup>2</sup> × g <sup>-1</sup>	66.3	78
Pore volume, mL × g <sup>-1</sup>	0.13	0.145
Micropore volume, mL × g <sup>-1</sup>	0.027	0.035
Average size, μm	59.5	58.5
<b>Chemical composition, %</b>		
Al <sub>2</sub> O <sub>3</sub>	52.9	53.5
SiO <sub>2</sub>	38.5	37.3
Na <sub>2</sub> O	0.24	0.18
<b>Metal content, %</b>		
Fe	0.49	0.5
Ni	0.29	0.43
V	0.16	0.25



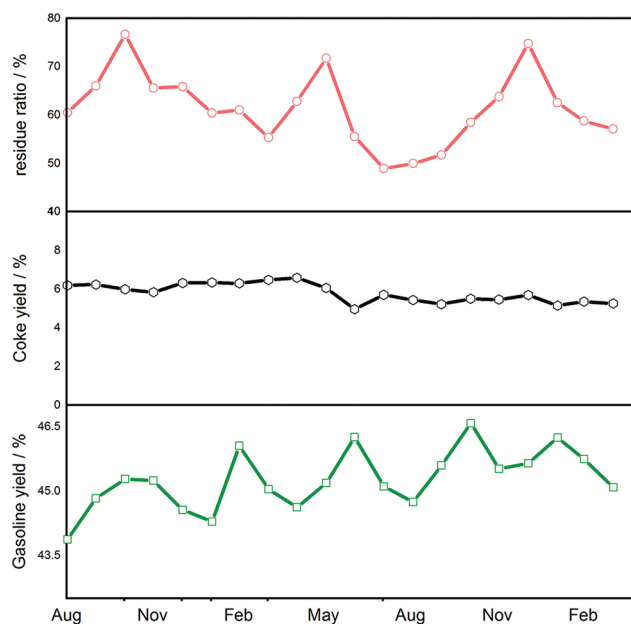
**TABLE 5. Product distribution and properties in blank calibration and summary calibration**

	Blank calibration	Summary calibration
<b>Product distribution, %</b>		
Dry gas	2.73	2.24
LPG	15.89	15.97
Gasoline	44.87	45.9
Diesel	20.21	20.97
Recycle oil	5.42	4.29
Slurry	3.7	3.79
Coke	7.48	7.18
Liquid yield, %	80.97	82.84
Conversion, %	70.67	70.95
Selectivity of gasoline	0.635	0.647
Selectivity of coke	0.106	0.101
<b>Properties of gasoline</b>		
Aromatics	25	23.2
Alkene	20.3	24.8
Alkane	54.7	52
Benzene	0.5	0.4
RON	90.4	90.8
MON	80.4	80.5
<b>Properties of slurry</b>		
Density, kg × m <sup>3</sup>	1034.3	1074.8
<b>Hydrocarbon fraction</b>		
Alkane, %	23.1	15.3
Aromatics, %	48.9	60.8
Gum, %	26.4	21.3
Asphalt, %	1.6	2.6

tribution of products, which can be found clearly in terms of the variation of the yields of gasoline and coke.

It should be noted that the product distribution could vary depending on the extent of reactions. Therefore, a more rational reflection of the product distribution should be selectivity. As shown in **TABLE 5**, compared to the previous catalyst<sup>b</sup>, the new catalyst<sup>a</sup> shows a better performance in product distribution with a 0.012% increase in the selectivity of gasoline and a 0.005% decrease of coke. The main properties of stabilized gasolines during the calibration are also shown in **TABLE 5**. The volume fraction of aromatic compounds is decreased from 25.0% to 23.2%, while the volume fraction of alkenes is increased by 4.5%. The amount of benzene is barely changed. The RON of stabilized gasolines is also increased by 0.4%.

All other properties meet the basic criteria, as well. The properties of slurry are also provided in **TABLE 5**. The density of slurry in the summary calibration is higher. The weight fraction of alkanes is decreased to 7.8% while that of aromatic hydrocarbons is enhanced to 11.9%; the ratio of both gum and asphalt rises, as well. The aforementioned results indicate an increase in the reaction depth, which confirms the ability of the new catalyst to improve catalytic activity.



**FIG. 5.** Monthly statistical data of residue ratio (red), gasoline yield (green) and coke yield (black).

**Distribution of FCC products and their properties.** To illustrate the potential of the new catalyst, monthly statistical data from 2019 to 2021 has been provided here, including the residue ratio in raw materials and the yields of gasoline and coke. As shown in **FIG. 5**, although the residue ratio fluctuates between 40% and 90%, the yields of gasoline and coke remain quite stable. The average yield of gasoline is ~45.5% and the yield of coke is only ~5.8%. With the high residue ratio in the raw materials, the cost of raw materials for the FCC process would be reduced by almost \$1,400/yr.

**Takeaways.** Because FCC raw materials are trending heavier, the need for a more efficient catalyst for the catalytic cracking of polycyclic naphthenes is increasing rapidly. With an improved design of the zeolite material and matrix, the new catalyst<sup>a</sup> shows promise for industrial applications. The yield of gasoline could reach 55.3% while the yield of coke is only ~5.8%, assuming an average residue ratio of 61.1% in the raw materials. **HP**

## NOTES

<sup>a</sup> SINOPEC'S ROC-1

<sup>b</sup> SINOPEC'S RICC-1

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## Refinery catalyst selection: Facts and fictions every refiner should know

Most refiners carefully evaluate their refining catalysts to ensure maximum benefits over the catalyst cycle length. Without a doubt, pilot plant testing is the best method to evaluate true catalyst performance. Often, the incremental catalyst cost is trivial compared with the economic benefits from improved catalyst performance.

To the authors' surprise, many refiners only consider testing some refining catalysts, such as hydrocracking, fluid catalytic cracking (FCC) or naphtha reforming units. This seems a reasonable line of thought, as these refining units are the critical profit makers of a typical refinery. So, why risk not testing?

Conversely, these refiners somehow believe testing other refining catalysts (e.g., diesel hydrotreating catalysts) is unnecessary. They argue that other refining catalysts are less critical and a paper-based evaluation is usually sufficient. This notion seems sensible on the surface, and many refiners follow this practice. However, is this really the case? Should refiners consider an 86,000-bpd diesel hydrotreater (like the one shown in **FIG. 1**) as not critical? Where is the line defining the criticality? Is a paper-based evaluation even a valid method? This article will answer these questions and emphasize why refiners should remain skeptical about skipping refinery catalyst testing.

**Reliance on a paper-based catalyst evaluation.** Many refiners think that comparing catalyst proposals from different catalyst vendors is a completely valid evaluation technique. However, this is flawed approach.

A typical catalyst proposal is the result of a proprietary kinetic model developed by an individual catalyst vendor. Although most (if not all) kinetic models share the

same core principles (e.g., Langmuir-Hinshelwood kinetics), each of them is unique if you look further into the assumptions and the details. Also, these kinetic models are not 100% accurate, so they are likely to yield different results despite the same feed properties.

Secondly, the feed properties provided by the refiner in the catalyst tender documents are mostly incomplete, inconsistent with each other or even over-specified. In the authors' experience, a set of feed properties is often a mix of data from various sources (e.g., original design data plus past operating data), as shown in **TABLE 1**.

It is not uncommon to see catalyst vendors making certain feed assumptions (typically based on institutional knowledge) during the feed characterization step (e.g., nitrogen, sulfur or aromatics distribution). A catalyst vendor might assume 35% of total nitrogen is basic nitrogen for Middle Eastern crudes while another uses  $\frac{1}{3}$  as an assumption. Which number is more accurate? How can we know if all catalyst vendors are adopting the same assumptions? Additionally, a typical crude diet is often a mix of various crudes from all around the world, and not only from a specific region. What if South American or West African crudes are dominant in the crude slate?

To add to the challenges, some catalyst vendors are more aggressive than others with their yield estimates. It must be remembered that a catalyst vendor's priority is to secure the sale. The authors have experienced cases where it became apparent that a catalyst vendor "tuned" its kinetic model to produce yields for its proposal that were more attractive. For example, a diesel hydrotreating catalyst vendor once proposed an almost nil offgas yield to a refiner without justifying or explaining this

anomaly. When challenged, the catalyst vendor just stated that it was the result of the kinetic model. To add insult to injury, the same catalyst vendor also proposed a suspiciously aggressive diesel product density (e.g., a much lower than usual diesel density). Although the same catalyst vendor later revised the new diesel density because the refinery expressed strong disbelief in the performance predictions, the vendor did not make any changes in aromatic contents in the diesel product and overall hydrogen consumption. The illogical revision was clear proof that this catalyst vendor deliberately tuned the catalyst performances presented in its proposal.

Without a reasonable explanation from the catalyst vendor regarding the "too good to be true" catalyst performance, the refiner decided to negatively weigh the results from the abovementioned catalyst vendor due to the uncertainty over the



**FIG. 1.** The diesel hydrotreater is one of the most important-yet-ignored refining units when it comes to refinery catalyst testing.



catalyst performance claims, resulting in the other bidders coming out ahead in the catalyst evaluation. However, how did the refiner know the vendor did not offer decent catalysts without pilot plant testing? While the estimates might be suspicious,

the catalyst R&D and actual performance might actually prove accurate.

Another example of how vendors may “manipulate” kinetic models is an accidental internal email in a catalyst company that discusses how to alter the original

pretreating temperature to make it believable during a hydrocracking catalyst bidding. This catalyst vendor later realized that the refinery contact was mistakenly included in the internal communication, although that contact never mentioned it.

These real stories are perfect examples of how refiners should always challenge the data presented in vendors’ proposals and how paper-based evaluations can be highly subjective.

Inherent flaws in paper-based catalyst evaluations exist and should be avoided, even when selecting naphtha hydrotreating catalysts. The authors have seen a naphtha hydrotreating unit that chronically suffered from off-specification product due to sulfur recombination reactions as a result of lower-than-expected catalyst activity (e.g., the reactor temperature exceeded the olefin saturation equilibrium). In another example, a kerosene hydrotreater with more than 150% of gas plus overhead liquid products—compared to the design (and catalyst specification) and at much lower reactor temperatures than the design—overloaded the top section of the stripper column.

**The myth of hydrocracking catalyst selection.** It is vital to test hydrocracking catalysts to reduce the risks of selecting a suboptimal hydrocracking catalyst package. As this major conversion unit is a significant profit center, a slight performance gap can easily cause multi-million-dollar losses. Nonetheless, the risk level associated with hydrocracking catalyst selection is not necessarily higher than other refining catalysts, as discussed in the following sections.

Clear distinctions exist between good and average/poor hydrocracking catalysts. As demonstrated in **FIG. 2**, catalyst Package C is clearly the best by both paper-based and pilot plant-based evaluation. While Package E seems a relatively weak second-best on paper, it performed well and almost won in the pilot plant testing—a \$10 MM/cycle benefit gap, although seemingly significant, is considered relatively close in hydrocracking. According to the authors’ survey, many refiners agree that the catalyst vendors that designed catalyst Packages C and E are technically fine based on past operating experiences.

Conversely, catalyst Packages A, B and D are inferior on both paper and pilot plant testing. The only difference is

**TABLE 1. An example of feed properties from a real bid tender for a hydrocracking catalyst package with the corresponding data sources**

Property	Test method	VGO	Data source
Specific gravity at 15°C	ASTM D4052	0.9012	Historical data—Current cycle average
Sulfur, wt%	ASTM D4294	0.42	Historical data—Current cycle average
Nitrogen, ppm wt%	ASTM D4629	1500	Design data
CCR, wt%	ASTM D4530	1.35	Design data
Heptane insoluble (C <sub>7</sub> ), wt%		0.1	Design data
Distillation (SIMDIST)	HT SIMDIST or ASTM D1160		Historical data—Current cycle average
IBP, °C		274.7	Historical data—Current cycle average
T5, °C		349.4	Historical data—Current cycle average
T10, °C		374.4	Historical data—Current cycle average
T30, °C		423.1	Historical data—Current cycle average
T50, °C		455.9	Historical data—Current cycle average
T70, °C		494	Historical data—Current cycle average
T90, °C		545.7	Historical data—Current cycle average
T95, °C		565.4	Historical data—Current cycle average
FBP, °C		605	Historical data—Current cycle average
Recovery at cracked temperature, %		100	Historical data—Current cycle average
Metal, mg/kg			
Ni	AAS by ICP or IP 501/03	0.4	Historical data—Worst case
V	AAS by ICP or IP 501/03	0.07	Historical data—Worst case
Na	AAS by ICP or IP 501/03	0.42	Historical data—Worst case
Fe	AAS by ICP or IP 501/03	0.22	Historical data—Worst case
Al	AAS by ICP or IP 501/03	0.23	Historical data—Worst case
Si	AAS by ICP or IP 501/03	0.68	Historical data—Worst case
As	UOP 946-96 (ICP-HG)	0.02	Historical data—Worst case
Hg, ng/g	UOP 398-000	2	Historical data—Worst case
Total aromatics, %m/m	SMS 2783	15.3	Historical data—Worst case
Mono		4.18	Historical data—Worst case
Di		3.39	Historical data—Worst case
Tri		4.08	Historical data—Worst case
Tetra+		3.65	Historical data—Worst case

**TABLE 2. A list of metals commercially used in hydrocracking catalyst manufacturing and their attributes**

Metal	Active form	Hydrogenation strength	Note
Co-Mo	Sulfided	–	Rarely seen
Ni-Mo	Sulfided	–	Less popular
Ni-W	Sulfided	Base	Most popular
Pd/Pt	Reduced	+	Typically used in the 2nd stage, requires low-sulfur environment

that while catalyst Package D offered the lowest cycle benefit on paper, it exhibited equivalent or better potential in pilot plant testing when compared to catalyst Packages A and B.

These results are supported by technical factors. One is the choice of metals. Principally, hydrocracking catalysts are bi-functional, comprising cracking and hydrogenation functions. For the cracking function, various blending ratios of amorphous silica-alumina (lower acidity/activity) and zeolites (higher acidity/activity) are possible. Concurrently, several metal choices with different hydrogenation strengths are also available, as summarized in **TABLE 2**. Catalyst manufacturers can adjust the ratio between the catalyst's cracking and hydrogenation strength to optimize overall catalyst activity and selectivity. A higher hydrogenation-to-acidity strength ratio results in better middle distillate yield, while a lower ratio produces more naphtha.<sup>1</sup>

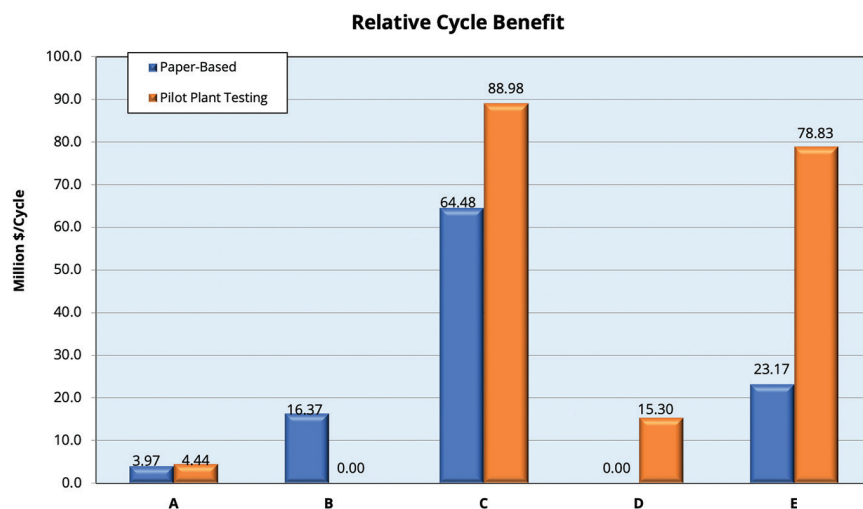
In this example, catalyst Package B utilized nickel-molybdenum (Ni-Mo) as the hydrogenation function for the proposed hydrocracking catalysts, while others relied on nickel-tungsten (Ni-W). As Ni-W is stronger than Ni-Mo when it comes to hydrogenation, Ni-W-based hydrocracking catalysts can better preserve primary cracking products (e.g., kerosene and diesel) by suppressing secondary cracking, assuming the same type of zeolite and zeolitic content, as illustrated in **FIG. 3**. This observation is in line with the fact that catalyst Package B achieved the lowest middle distillate yield during the pilot plant testing, among other factors. Additionally, hydrocracking catalysts with a stronger hydrogenation function help improve product qualities [e.g., smoke point, cetane number and unconverted oil (UCO) viscosity index].

Conversely, the top performer, the supplier of catalyst Package C, claimed to have a high degree of mesoporosity in the zeolite framework (**FIG. 4**). This structural advantage aids molecular diffusion and helps reduce the degree of secondary cracking (i.e., the primary cracking products are released more rapidly from the zeolite network).<sup>2</sup> Additionally, this catalyst manufacturer employs a specially engineered catalyst shape where the diffusion path length is shorter than conventional ones, therefore minimizing over-cracking. Lastly, this competitor utilizes

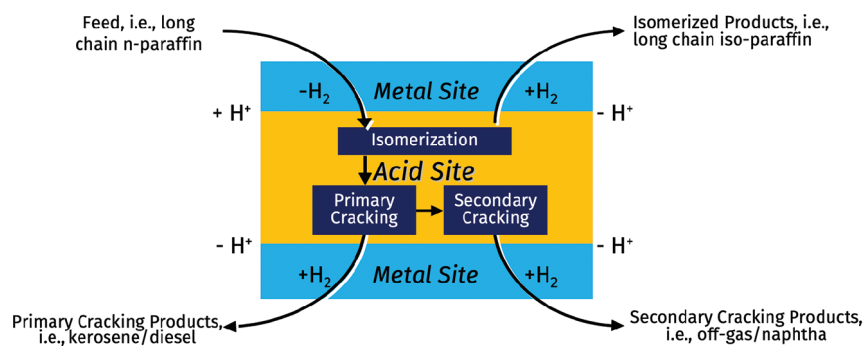
stronger Ni-W as the hydrogenation function for its hydrocracking catalysts. These described catalytic features partially explain why the company outperformed other hydrocracking catalyst manufactur-

ers in terms of the total liquid and middle distillate yields.

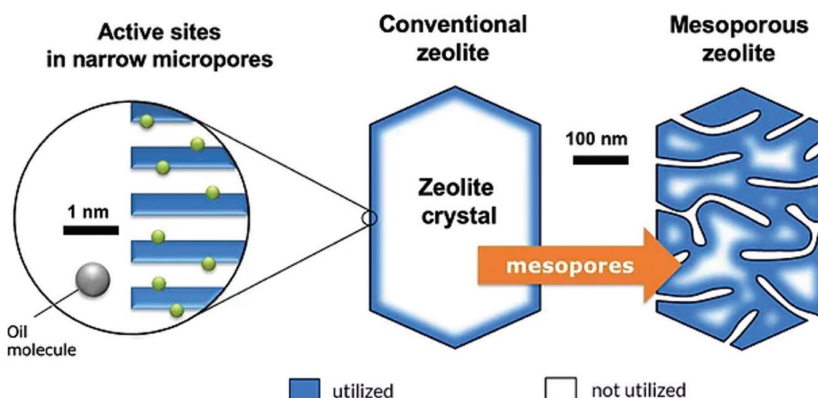
Although this is just one example, the authors have seen several hydrocracking catalyst evaluations with similar re-



**FIG. 2.** Relative cycle benefit of various hydrocracking catalyst packages for a 54,000-bpd hydrocracker. Catalyst Package D was a baseline for a paper-based evaluation, while catalyst Package B took the same role in pilot plant testing.



**FIG. 3.** Typical hydrocracking reaction pathways: both metal and acid sites are essential to complete the hydrocracking process.



**FIG. 4.** Mesoporization of the zeolite structure can improve the acid site accessibility and reduce the degree of over-cracking in heavy oil hydrocracking by shortening the diffusion path length within the zeolite structure. Source: Zeopore Technologies.

sults (i.e., the winner on paper is also the winner in pilot plant testing). In other words, selecting catalyst Package C over Package E is simply choosing a very good catalyst package over an almost-as-good catalyst package. In truth, selecting catalyst Package E over Package C for alternative reasons is still not a bad choice in terms of economics.

In most cases, catalyst vendors must guarantee key performance parameters (e.g., product yield or hydrogen consumption). As such, it would be risky for them to over-exaggerate their proposal just to win the contract. When the catalyst vendors know that the catalyst evaluation is pilot plant-based, it provides more incentive to be more realistic with the yield estimates in their proposals.

For instance, if the middle distillate yield based on the original estimation is 70 wt% for a middle distillate selective application, it can be almost certain that no catalyst vendor would aggressively put 75 wt% in the catalyst proposal—it would obviously fail during the pilot plant testing or performance test run, and random excuses will be insufficient. In the authors' experience, the middle distillate yield gap between “the best” and “the worst” hydrocracking catalyst in the market could be greater than 5 wt%. Therefore, the hydrocracking catalyst price tends to play a minor role in the hydrocracking catalyst evaluation.

For these reasons, the risks associated with hydrocracking catalyst selection are

not necessarily as high as perceived. At a minimum, this prevents the selection of poor hydrocracking catalysts. Nonetheless, pilot plant testing is still the best method to evaluate hydrocracking catalysts, as the gap between the best and second-best hydrocracking catalyst can be significant. More importantly, it is also possible that the catalyst ranking might change if the catalyst performances are close (i.e., catalyst Packages C and E in **FIG. 2**).

**Higher-activity pretreating catalysts improve the middle distillate selectivity of hydrocrackers.** In principle, an overall conversion is a result of both pretreating (hydrotreating) and hydrocracking reactions. The primary focus of the pretreating section is to lower the organic nitrogen concentration to an acceptable level (typically < 50 ppm for modern designs) to prevent nitrogen inhibition effects in the hydrocracking section. In parallel, the pretreating reactor also removes other contaminants like metals, sulfur, oxygen and halides, as well as saturates olefins and aromatics (**FIG. 5**).

These hydrotreating reactions reduce the boiling point of the original hydrocarbon molecules, also known as pretreating conversion (**FIG. 6**). The gross pretreating conversion can be up to 30% for modern pretreating catalysts with a relatively low nitrogen slip target (e.g., < 10 ppm). In other words, the hydrocracking conversion could be as low as 69% for a fixed overall conversion of 99%.

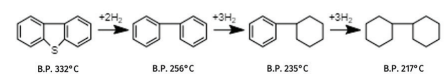
Targeting a higher pretreating conversion improves product selectivity, especially middle distillates, as pretreating catalysts are typically much more middle distillate selective than hydrocracking catalysts. A higher-activity pretreating catalyst saturates more aromatic compounds (increased hydrogen consumption), thus higher pretreating conversion and better overall middle distillate selectivity, assuming the same nitrogen slip target. With a lower pretreating temperature, the extent of thermal cracking (which results in poor liquid yields) will also be reduced.

Additionally, higher-activity pretreating catalysts will permit refiners to operate at the lower nitrogen slip level, allowing the addition of more middle distillate selective hydrocracking catalysts (lower zeolitic content).

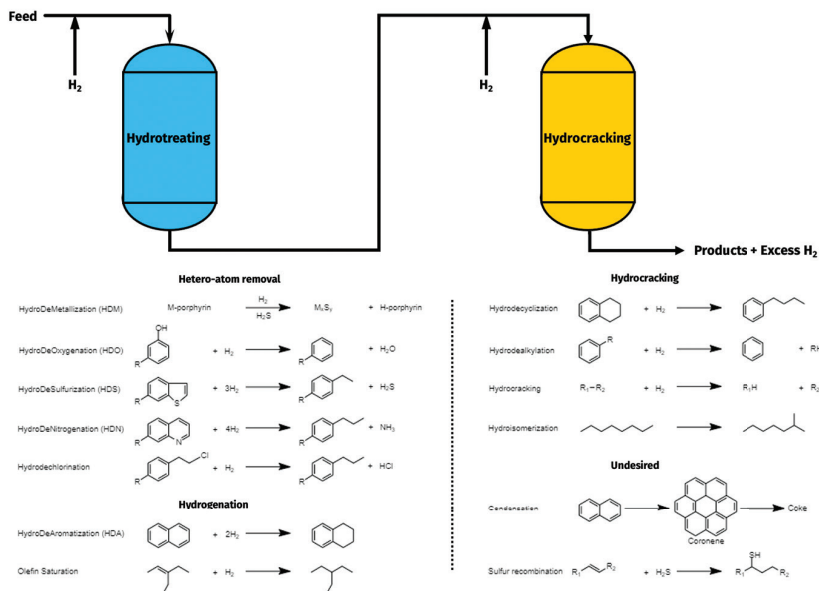
Unfortunately, this best practice is not always the case. The authors once tried adding a small layer of ultra-high activity trimetallic unsupported catalyst (Ni-Mo-W) into a pretreating reactor to improve the overall middle distillate yield, as there was excess hydrogen available then. According to the catalyst supplier, this modification should enhance the overall middle distillate yield by another 0.5 vol%. As this unsupported catalyst had just been recently launched to the market and had few references, the authors requested the catalyst supplier to conduct pilot plant testing to confirm the benefit claims.

In contrast with the already explained conversion balance principle, the pilot plant testing campaign revealed that the trimetallic unsupported catalyst increased light ends production, thus reducing the overall middle distillate yield by 0.6 vol%. Although it also lowered kerosene and diesel density, the density improvement was nonetheless insufficient to compensate for the middle distillate weight yield loss. The catalyst vendor offered no clear explanation for this phenomenon—perhaps the vendor did not know, or it did not want to reveal flaws in its newly launched catalyst.

One hypothesis for this phenomenon



**FIG. 6.** A demonstration of how heteroatom removals and hydrocarbon saturations reduce hydrocarbon boiling points. In this case, a di-benzothiophene (DBT) molecule is hydro-treated and ends up as bi-cyclohexane (BCH).



**FIG. 5.** Reaction classes in a typical hydrocracking process.

is that the trimetallic unsupported catalyst developed by the concerned catalyst supplier promoted excessive C-C bond cleavage by metal components, also known as hydrogenolysis. This metal-catalyzed hydrogenolysis mechanism results in high  $C_1$  and  $C_2$  hydrocarbons yields, along with light n-paraffins and a near absence of iso-paraffins.

Fast forward to the subsequent bidding: this catalyst supplier decided not to include this trimetallic catalyst in the offered loading scheme, but returned to a conventional Ni-Mo hydrotreating catalyst. This implies a performance trade-off in the supposedly high-performing trimetallic hydrotreating catalyst. Otherwise, the supplier would have continued to propose it in the following cycle to gain performance advantages in the bidding.

**“There is no need to test diesel hydrotreating catalysts.”** The authors actually heard a diesel hydrotreating catalyst vendor say this after a refiner suggested that pilot plant testing might be used to better evaluate diesel hydrotreating

catalysts in the next bid process.

The vendor’s reasoning was that such a “less critical refining unit” did not require pilot plant testing. The authors disagree with this catalyst vendor and question whether they will lose a bid again in a fair process.

In contrast with hydrocracking units, diesel hydrotreaters produce much lower light-ends yields (gas and naphtha), mainly from hydrotreating reactions of sulfur, nitrogen, olefin and aromatic compounds (see the previous section). In diesel hydrotreating applications, hydrocracking reactions are negligible unless dewaxing catalysts (zeolitic-based) are used for cloud point reduction.

Hydrotreating conversion is less than 3 wt% without dewaxing, although a decently cut straight-run feed (e.g., from a crude distillation column) would easily achieve > 98 wt% diesel yield. This is one reason the selectivity of diesel hydrotreating catalysts is rarely discussed. A more popular discussion topic is the optimal ratio between Co-Mo and Ni-Mo catalysts and how to stack them in a reactor.

It is difficult for refiners to accurately quantify the light-ends yields in an operating environment due to inherent flow measurement errors. Naphtha flow is only a tiny fraction of total product flow, while offgas flow is notoriously inaccurate due to varying gas composition. It is not uncommon to see a raw mass feed flowrate with a flow reading less than that of the diesel product.

As discussed previously, the diesel yield usually lies somewhere between 98 wt% and 100 wt% for most straight-run diesel hydrotreaters, which is actually less than the possible orifice flowmeter error of  $\pm 3$  wt%–5 wt%. Unsurprisingly, an error in diesel flow measurement could easily mask a lower-than-expected diesel yield. In the authors’ experience, some catalyst vendors have exploited this loophole to benefit them in catalyst biddings by proposing an unrealistic diesel yield. The authors once saw a catalyst vendor that boldly proposed 99.9 wt% diesel yield for ultra-low sulfur diesel (ULSD) operation with reasonable sulfur and aromatic contents in the feed.



**TABLE 3. Examples of how independent diesel hydrotreating catalyst testing help improve refining margins**

Refiner	Catalyst decision	Issue	Performance benefit	Catalyst cost savings
North American refinery	North American supplier replaced European supplier	Short cycle undiagnosed by incumbent	6-mos cycle to 2-yr cycle	\$2 MM
North American refinery	European supplier replaced European supplier	Catalyst testing showed opportunities	3-tier improvement	\$1 MM
North American refinery	European supplier replaced European supplier	Catalyst testing showed opportunities	2-tier improvement	\$200,000 plus price cuts on other catalysts
North American refinery	European supplier replaced European supplier	Short cycle undiagnosed by incumbent	2-tier improvement	\$330,000 plus price cuts on other catalysts
North American refinery	European supplier replaced European supplier	Catalyst testing showed opportunities	1- tier improvement	\$600,000
European refinery	North American supplier replaced European supplier	Short cycle undiagnosed by incumbent	1-tier improvement	\$500,000

Notes: 1) 1-tier improvement = 5°C reduction in start-of-run temperature

Source: Hoekstra Trading LLC

Another popular excuse is the actual feed quality, which is never exactly the same as what is in the bid tender—catalyst vendors can always argue that the performance gaps are from deviations in feed qualities. Any deviations in product properties (e.g., diesel density) will be disputed.

In many cases, it is difficult for refiners to claim any penalties (usually not worth it, compared with potential damages) due to a failed unit test run. The authors have seen a catalyst vendor that failed every performance test run over 6 yr that was selected repeatedly just because its customer relied on a paper-based evaluation to choose diesel hydrotreating catalysts.

For the described reasons, diesel hydrotreating catalyst selection is no less critical than other refining catalysts; it is difficult to distinguish the best catalyst package from the average/poor ones without pilot plant testing due to different kinetic models used in performance predictions and the potential for the catalyst vendor sales team to over-exaggerate the performance of their catalysts. Rather than differentiating the performances of various catalysts, refiners may potentially be wasting their time trying to identify frequently unmeasurable/debatable gaps in the operating environment.

According to Hoekstra Trading LLC, a one-tier improvement in performance or a 5°C reduction in the start-of-run temperature is worth \$1 MM/yr–\$5 MM/yr in a typical ULSD unit (TABLE 3). A lower start-of-run temperature means a higher feedrate, the ability to use more difficult (cheaper) feeds in the ULSD unit, and lower light gas yields from less severe thermal cracking. The benefits of a better diesel hydrotreating catalyst package, especially

for a larger unit, easily outweigh the service fee of an independent pilot plant testing program. Generally, the service fee for diesel hydrotreating applications is only half of that for hydrocracking catalyst testing.

**Naphtha reforming is a monopoly business.** The authors have seen one company have repeated success in pilot plant testing, so it could be assumed that pilot plant testing is unnecessary since every benchmarking campaign the authors have seen by this company had the same result. This might indicate that this company is ahead of its competitors regarding naphtha reforming catalyst development, but an expert in refinery catalyst testing detailed cases where other naphtha reforming catalyst suppliers also had successful pilot plant testing campaigns. Naphtha reforming catalysts perform differently with varying feeds, operating conditions and product specification requirements.

Importantly, all catalyst suppliers continue to develop their products, and there is no guarantee that today's prominent market leaders will retain their position. Pilot plant testing is still highly recommended for the evaluation and selection of the best naphtha reforming catalyst to suit refiners' applications.

**Takeaways.** While both conventional and high-throughput approaches can be used to distinguish the best-performing refinery catalyst from average ones, the high-throughput technique offers some great advantages over the conventional method in several circumstances.<sup>3</sup>

The author's company's high-throughput platform<sup>a</sup> with 16 parallel reactors produces consistently high data quality in

terms of repeatability, reproducibility, scalability and mass balance quality, thanks to the company's patented gas distribution technology, active liquid distribution (ALD) system and single-pellet string reactor (SPSR) catalyst loading approach. Additionally, the required catalyst volume is less than 1 mL. As such, the required catalyst and feed sample volumes are minimal, making the platform<sup>a</sup> one of the most cost-effective commercial catalyst testing platforms available. **HP**

#### NOTES

<sup>a</sup> Avantium's Flowrence<sup>®</sup> platform

#### ACKNOWLEDGEMENT

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#### LITERATURE CITED

Complete literature cited available online at [www.HydrocarbonProcessing.com](http://www.HydrocarbonProcessing.com).

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## The other sulfides: Organic sulfur species in amine solvents

This article examines the behavior of carbonyl sulfide (COS),  $C_1$ – $C_5$  mercaptans ( $R_1SH$ – $R_5SH$ ), methyl ethyl sulfide (MES), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) in amine solvent systems. The objective here is to explore the current state of open industry knowledge in this area and compare it to gathered field test data. This article will highlight what is and what is not known and is a good starting point for future study on this topic, as not much field data has been previously published. The article contains:

1. A review of the chemistry of organic sulfur species in amine systems
2. Trending and analysis of key operating parameters for data from 50 industrial amine solvent absorbers
3. A study of the organic sulfur challenge at a European refinery.

Optimizing the removal of organic sulfur species can eliminate the need for, or reduce the size of, downstream gas conditioning units in new facilities. In existing systems, this offers the advantage of extending cycle times on molecular sieves and reducing the consumption of caustic and the volume of mercaptide and disulfide waste streams requiring disposal.

**Note:** The removal of sulfide species from liquefied petroleum gases (LPG) through liquid-liquid extraction is not covered here. Carbon disulfide ( $CS_2$ ) is also not included in this study, as its presence in gas streams is thought to be mostly limited

to tail gas treating units (TGTUs). The authors' company has extensive field data for LPG treaters and  $CS_2$  removal, and this data will be the subject of future work.

**Background.** The non-hydrogen sulfide ( $H_2S$ ) sulfide species COS,  $C_1$ – $C_5$  mercaptans ( $R_1SH$ – $R_5SH$ ), methyl ethyl sulfide (MES), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) are frequently present in hydrocarbon streams in the oil, natural gas and biogas industries and are commonly called 'organic sulfur.' The behavior of organic sulfur species in amine systems is generally poorly predicted but can have a major impact on plant operations. This has been highlighted during work on two recent projects.

The first, an ultra-sour natural gas plant in the Middle East, contained ~1,000 ppmv of non- $H_2S$  sulfide in its feed. Units were built downstream of the amine absorber to remove the organic sulfur from the gas product. When the authors' company commissioned and performed guarantee testing on the plant, it became apparent that the amine system was almost entirely removing the organic sulfur species from the gas. This effectively rendered the downstream mol sieve organic sulfur removal units unnecessary at start-of-run (SOR) operating conditions. Details on this project are provided by Schulte, *et al.*<sup>1</sup>

The second project was a European refinery, Preemraff Lysekil, where compliance with strict internal and governmental environmental standards on stack sulfur dioxide ( $SO_2$ ) emissions was limit-

ing throughput. The refinery initiated an analytical testing program to determine the primary sources of the  $SO_2$  emissions. This was traced back to the treated gas from a specific amine absorber (one of the 12 onsite). Specifically, the visbreaker LPG fraction (which contains significant mercaptan sulfur) was being added into the feed to this absorber—when burned, this fuel gas accounted for a large portion of the refinery sulfur emissions. Similar emissions resulting from mercaptans have subsequently been found at four other refineries in Europe and three in the U.S., all of which also vaporize a large portion of the visbreaker/coker LPG fraction into their refinery fuel gas.

Both projects experienced a significant economic impact because the behavior of organic sulfur species in amine systems is not well-developed in industry. This article will present the information available to the industry and from the authors' company, and highlight areas where work is needed to improve understanding.

**The theory of organic sulfur species removal with alkanolamine solvents.** In an amine absorber tower, the gas being treated is contacted counter-currently with an amine solvent. These solvents are alkaline in nature and remove target species—which are acidic in aqueous solutions—such as  $H_2S$  and carbon dioxide ( $CO_2$ ) by chemical absorption. Non-dissociating species (e.g., hydrogen, nitrogen, methane) can also be partially absorbed in the amine solution through

physical absorption, which is predominantly a function of pressure, temperature, residence time and solubility.

A good review of the available prior work on the removal of COS and lighter mercaptans in amine systems can be found in literature by Kohl and Nielsen.<sup>2</sup> Reports on removal rates are given by other authors, but these are drawn from a very limited number of data points—in many cases, the results are from a single installation. These numbers are summarized in TABLE 1. To the authors' knowledge, there is little information on heavier mercaptans (C<sub>4</sub>SH and higher), MES, DMS or DMDS in open literature.

The following pathways for organic sulfur species removal in an amine system are possible:

1. Physical absorption
2. Chemical absorption (acid-based reaction)
3. Direct chemical reaction with amine
4. Direct chemical reaction with water (hydrolysis) for some species (COS and CS<sub>2</sub>)

5. Condensation or absorption into a separate liquid hydrocarbon phase
6. Conversion via reaction with other species in the gas or amine solvent solution.

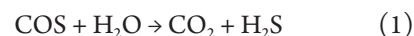
With multiple organic sulfur species and multiple pathways in an already-complex system, many gaps exist in industry knowledge with respect to how, and how much of, an organic sulfur species will be removed in a particular amine system.

Physical absorption is driven by the difference in each species' partial pressure in the hydrocarbon phase being treated and in the aqueous amine phase. Absorption will depend on temperature, pressure, contact time and solubility. Organic sulfur species are normally only present at ppm levels and pressure is thus not a significant driving force for their removal.

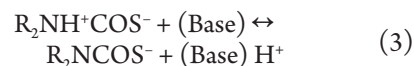
In addition to physical absorption, mercaptan sulfur species will also undergo chemical absorption, reacting with amine to form mercaptide salts. The resulting system is quite complex to model mathematically and has previously been described for R<sub>1</sub>SH–R<sub>4</sub>SH mercaptan

sulfur by Jones, *et al.*<sup>7</sup> The other organic sulfur species are not known to dissociate. Mercaptan competes with H<sub>2</sub>S and carbonic acid (H<sub>2</sub>CO<sub>3</sub>) for chemical absorption by amine molecules. Protonated amine bound to sulfide or carbonate is not available for reaction with mercaptans and reduces the driving force for their removal. Until large amounts of H<sup>+</sup> ions are no longer being formed (once all the H<sub>2</sub>S and CO<sub>2</sub> are removed), the mercaptan removal by chemical absorption will be poor.

In the case of COS, it is believed by many in the industry that a hydrolysis reaction is the primary mechanism for its removal.<sup>2</sup> This reaction is shown in Eq. 1:

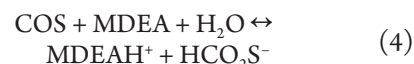


A zwitterion reaction mechanism for COS with primary and secondary amines was proposed by Little, *et al.*<sup>9</sup> in Eqs. 2 and 3:



This two-step reaction mechanism is comparable to that of the absorption of CO<sub>2</sub> by amines. It is comprised of a first step, where a COS-amine zwitterion is formed, and a second step, where the COS-amine zwitterion is deprotonated in the presence of a base (unreacted amine present in the solution).

For tertiary amines, Little, *et al.*<sup>10</sup> proposed the following (Eqs. 4 and 5):



The first reaction of COS with methyldiethanolamine (MDEA) to form protonated MDEA and monothiocarbamate is reversible and an order of magnitude faster than the irreversible second reaction. The overall reaction is very similar to hydrolysis. A comparison of the reaction rates of various amines with COS, adapted from the thesis of Little<sup>11</sup>, is shown in FIG. 1.

While prior research by Rahman, *et al.*<sup>12</sup> found no evidence for the direct reaction of methyl mercaptan with monoethanolamine (MEA), diethanolamine (DEA), diglycolamine (DGA), diisopropanolamine (DIPA) or MDEA, COS can react directly with MEA, DEA, DGA and possibly DIPA to form degradation products. The rate of degradation with COS

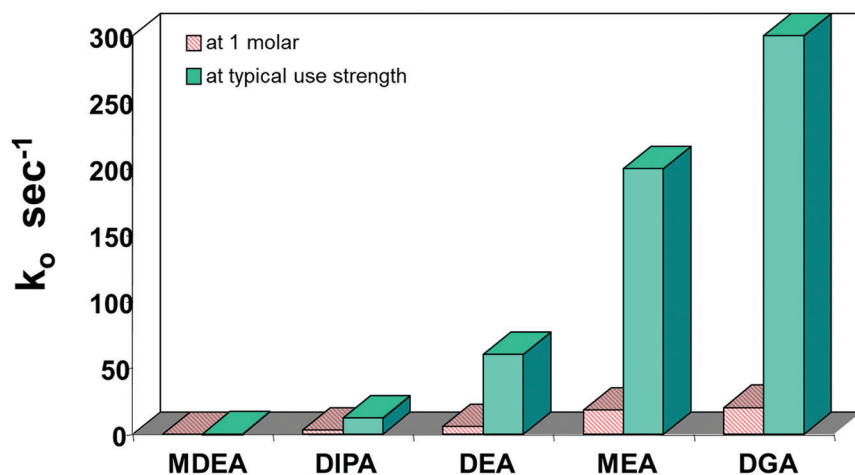


FIG. 1. Pseudo-first order rate constants for reaction of amine solvents with COS.<sup>11</sup>

TABLE 1. Percentage removal of various organic sulfur species by amines as reported in literature

Amine	R <sub>1</sub> SH	R <sub>2</sub> SH	R <sub>3</sub> SH	COS	Source
MEA/DEA	45–55	20–25	0–10	70–80	Butwell, <i>et al.</i> <sup>3</sup>
DGA	14	12	–	90	Huval and van de Venne <sup>4</sup>
DGA		98		–	Harbison and Dingman <sup>5</sup>
DGA		90		–	Kenney, <i>et al.</i> <sup>6</sup>
MDEA*	7	8	10		Jones, <i>et al.</i> <sup>7</sup>
MDEA				33	Seagraves <sup>8</sup>

\*45 wt% methyldiethanolamine (MDEA) with at least 0.07 mol/mol H<sub>2</sub>S loading

is significantly faster in primary (MEA, DGA) amines than in secondary and tertiary ones. In DGA, the degradation product [N, N bis(hydroxyethoxyethyl) thiourea abbreviated as BHEEU] is reversible in a reclaimer; therefore, COS degradation is primarily a concern in MEA systems where it converts MEA to diethanolurea, which is not reversible.

According to Dawodu,<sup>13</sup> COS reacts with DEA to form MEA, bis-hydroxyethyl imidazolidone (HEI), bis hydroxyethyl piperazine (BHEP), hydroxyethyl oxazolidone (HEOD), tris-hydroxyethyl ethylenediamine (THEED) and bis-hydroxyethyl ethylenediamine (BHEED). Butwell, *et al.*<sup>3</sup> reported that only 2% of COS in the feed gas reacted with DEA irreversibly, while removal of up to 80% is possible primarily through the hydrolysis reaction. DIPA is thought to degrade with COS, but the rate of reaction is slower than the time allowed for experiments to determine this.<sup>2</sup> DIPA is considered a suitable solvent for COS removal in conjunction with a physical solvent (i.e., the sulfinol-D formulation). Rahman, *et al.*<sup>12</sup> did not detect any reaction of COS with MDEA or dimethylethanolamine (DMEA).

While it is thought possible for COS to react directly with water, this reaction is too slow to be industrially relevant. Cantrell, *et al.*<sup>14</sup> applied Danckwerts' criteria<sup>15</sup> to show that the reaction of COS directly with water is not relevant in terms of available contact time on amine absorber trays.

Both COS and mercaptan sulfur removal are disadvantaged by the presence of H<sub>2</sub>S and CO<sub>2</sub> in the amine. Therefore, most of their removal is thought to be in the top part of an amine absorber after the bulk of the H<sub>2</sub>S and CO<sub>2</sub> have already been absorbed. Following from this theory, some industry rules-of-thumb have evolved:

1. The removal of organic sulfur only happens after most of the H<sub>2</sub>S and CO<sub>2</sub> have been removed. Anecdotal, columns with more contact stages have reported better removal. An example can be found in literature.<sup>11</sup>
2. Mercaptan and COS removal are favored by lower lean amine CO<sub>2</sub> and H<sub>2</sub>S loadings. Therefore, more regeneration (reboiler duty use) will be required.
3. Lighter mercaptans exhibit larger solubilities than heavier mercaptans in amine solutions. Heavier

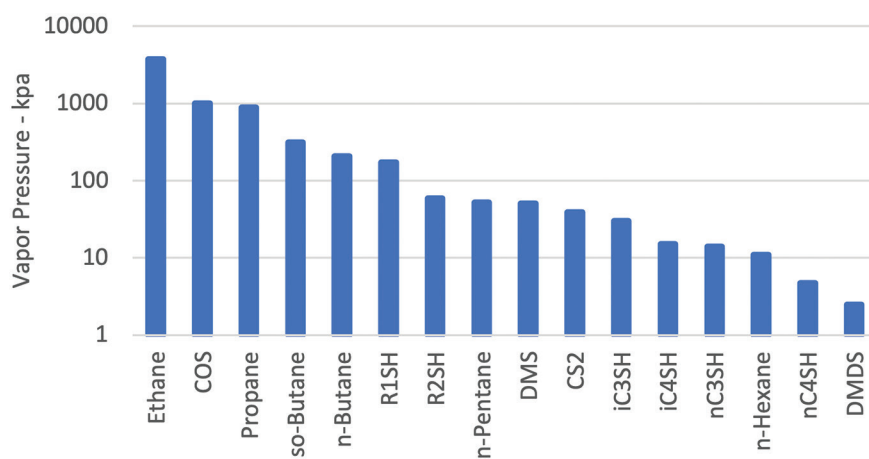


FIG. 2. Vapor pressures of possible feed components at 21°C.

mercaptans are increasingly non-polar (more hydrocarbon-like) with an increasing carbon number, therefore less soluble in the highly-polar aqueous amine.

4. Amine systems attempting to slip CO<sub>2</sub> (tail gas treating and acid gas enrichment units) will not have good organic sulfur removal, as significant absorption of CO<sub>2</sub> will be occurring in the top trays of the contactor, which will compete with organic sulfur removal.

Mercaptan has been shown to react with molecular oxygen in basic aqueous solutions under mild temperature and pressure conditions to form disulfides and peroxide or water.<sup>16</sup> Uncatalyzed conversion rates are slow, but a wide range of simple metal salts can serve this purpose, including Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, CoCl<sub>2</sub> and CuSO<sub>4</sub>, among others.<sup>17</sup> This reactivity is the basis for the Merox processes developed by UOP used to sweeten a wide variety of hydrocarbon products, from LPG to jet fuel. While Merox units use advanced proprietary catalysts for efficient conversion, the simple metal salts commonly encountered in amine-based treating units from the process of corrosion may act in a similar manner, if the unit suffers from oxygen incursion.

Experimental work by Borgeson<sup>18</sup> almost a century ago suggested that mercaptans could be formed from the reaction of H<sub>2</sub>S with some aldehydes, ketones, olefins, acetic and propionic acid. None of these experiments was done in an alkaline environment and mercaptan was detected only by odor due to the analytical limitations of the time.

Concurring with these observations, preliminary lab experiments by the authors' company led to the detection of mercaptan in the gas headspace above aqueous amine solutions mixed with methanol or acetone after pressurizing with H<sub>2</sub>S gas and heating to temperatures approximating those encountered in an absorber tower. While further investigation of these results is required, they suggest it may be reasonable to observe a change in the ratios or even an increase in concentration of organic sulfurs between the outlet and inlet of an absorber under certain conditions.

**The theory of organic sulfur phase partitioning.** One difficulty in deciding which amine is best suited to remove particular organic sulfur species is the question of exactly how it will partition in the various liquid and vapor streams in a refinery or gas plant. One method of determining sulfur species partitioning is via vapor pressure comparisons to associated hydrocarbon streams. FIG. 2 shows a log-scale bar graph of vapor pressure, in descending order, for components that may be present in a feed hydrocarbon stream.

As indicated by Likins and Hix,<sup>19</sup> when considering vapor pressures only, the chart shows that COS should distribute into the propane stream and possibly into an ethane/propane mix stream. Methyl mercaptan (R<sub>1</sub>SH) should distribute primarily into the n-butane stream with some going with both the i-butane and gasoline streams. Ethyl mercaptan (R<sub>2</sub>SH), DMS and CS<sub>2</sub> should end up primarily in the gasoline stream with only minor distribution into the n-butane stream. The other



heavier sulfur compounds should end up almost entirely in the gasoline stream.

In practice, contrary to the vapor pressure expectations of very little mercaptan partitioning into the propane stream, more than 50%–60% of the  $R_1SH$  has been measured there. COS indeed partitions between the ethane/propane mix and the propane stream.

Simulators also attempt to calculate partitioning based on available property data (critical properties, eccentric factors, regressed VLE data, etc.), but even with these data, simulators are challenged to match one another in key component partitioning predictions, perhaps because not all property data are valid.

Presently, in-plant analysis with sulfur-specific gas chromatograph testing capabilities is the best way to understand the partitioning of sulfur species and, ultimately, the quantity of each component in each hydrocarbon stream that must eventually be removed by the amine so-

lution. Feed-stream sulfur speciation and treated-stream sulfur speciation will characterize the true performance of the amine solvents in removing the various extended sulfur species in the plant.

## FIELD TEST DATA AND TRENDS

Gas compositions used to determine the figures presented in the following section come from samples collected on live plant sites. All samples were collected in sulfur-inert containers<sup>a,b</sup>. Samples were analyzed on proprietary gas chromatographs<sup>c</sup> (GCs) equipped with proprietary columns<sup>d</sup> and flame photometric detectors (FPD). The GCs were transported to site and calibrated in-situ with a traceable standard for all reported components.

**COS.** To render the trends more meaningful, data points with very little COS (< 4 ppm) were removed, as these are more likely to be errors due to sampling

and analysis. Cases where the amine solvent was significantly contaminated with another amine were also not considered. The data presented below come from five refinery fuel gas absorbers operating between 3.5 barg and 13 barg with inlet COS concentrations ranging from 4 ppmv–336 ppmv.

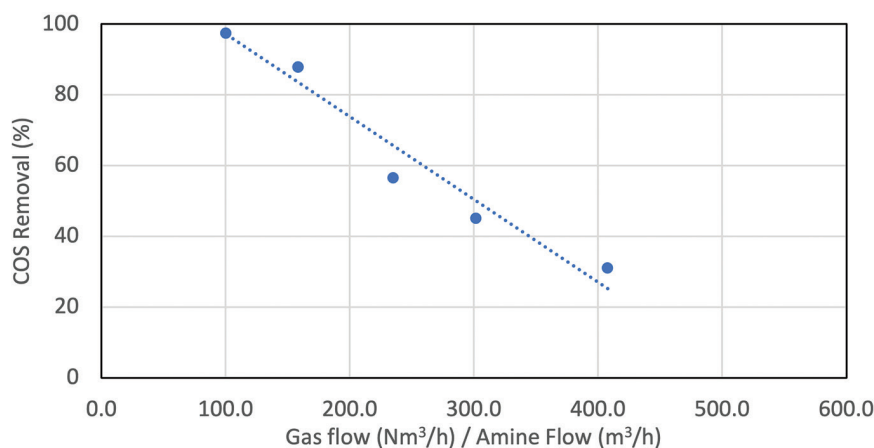
The removal of COS in DEA was trended against the following: absorber operating pressure, lean loading, rich loading, amine strength, amine temperature, simulated absorber maximum bulge temperature, inlet COS content and gas-to-liquid ratio. The removal of COS in DEA appears to have a strong linear correlation with the gas-to-liquid ratio, with other parameters having less impact. This is shown in **FIG. 3**.

For COS removal in MDEA, a linear correlation was found between the simulated temperature bulge in the absorber column and COS removal (**FIG. 4**). The data come from four refinery fuel gas absorbers, two TGTUs and two natural gas plant absorbers. The absorbers operated between atmospheric and 29 barg pressure, with the inlet COS ranging from 9 ppmv–522 ppmv. Absorber operating pressure, lean loading, rich loading, amine strength, lean amine temperature, inlet COS content and gas-to-liquid ratio did not show strong correlations (linear or otherwise) with COS removal.

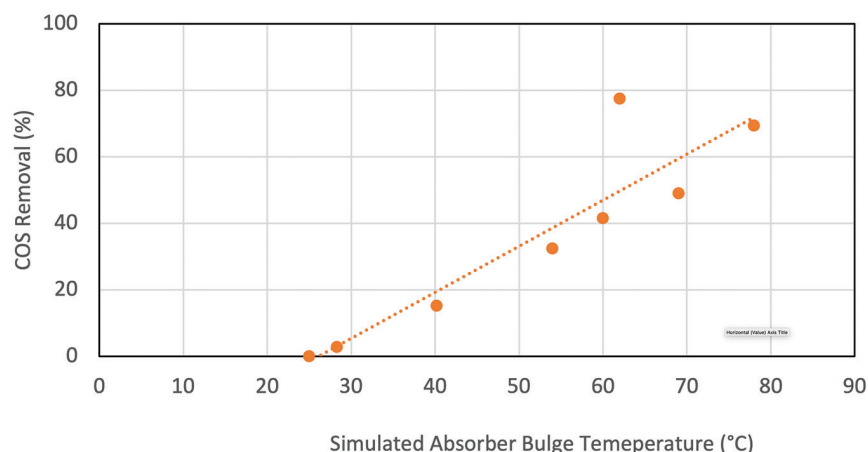
In TGTU absorbers, there is (generally) no significant temperature bulge in the absorber and amine flowrates are minimized to reduce  $CO_2$  absorption. Therefore, other factors may dominate COS absorption in TGTUs. Generally, not much COS is removed in TGTU absorbers.

**$R_1SH$ .** For primary and secondary amines, there was a very rough correlation between increased methyl mercaptan removal efficiency and smaller gas-to-liquid ratios (**FIG. 5**). **Note:** These are live plants and not controlled experimental environments. This was further investigated in a test run at Preemraff Lysekil on the T2904 visbreaker fuel gas absorber—a much stronger trend was observed, shown in **FIG. 6**. The removal of up to 80% of inlet mercaptan appears to be achievable with generic primary and secondary amines when low gas-to-liquid ratios are used in the column.

This trend has also been observed in literature. A paper presented by Dow<sup>20</sup> de-



**FIG. 3.** COS removal in DEA vs. absorber V/L ratio for five absorbers.



**FIG. 4.** COS removal in MDEA vs. simulated absorber bulge temperature for eight absorbers.

scribes an improvement in light mercaptan removal using an amine-only solvent blend when the gas-to-liquid ratio is decreased by ~40%. Further presentations by Dow and Spectra Energy<sup>21</sup> present data from a test run on the two trains at the SpectraJedney plant in Canada. These data show an increase in mercaptan removal efficiency with their hybrid amine and physical solvent with decreasing gas-to-liquid ratios and increasing numbers of contact stages. Additionally, work describing the industrial testing of hybrid amine-physical solvent by Total S.A.<sup>22</sup> at its Lacq plant in France describes decreasing the gas-to-liquid ratio by ~25% to obtain improved removal of methyl mercaptan with a DEA-thiodiglycol (TDG) mix.

There was no clear correlation of methyl mercaptan absorption in MDEA with any process parameters; removing 20% of inlet methyl mercaptan in the seven absorbers was (generally) being studied (FIG. 7).

**R<sub>2</sub>SH.** For ethyl mercaptan absorption by DGA, the trend of higher removal at lower gas-to-liquid ratios was once again observed (FIG. 8). This trend was not seen with DEA or MDEA.

Curiously, DEA and MDEA showed a trend of increased removal with decreased amine solvent strength (FIG. 9). This runs counter to conventional wisdom that higher amine strength will increase mercaptan removal. It is possible that ethyl mercaptan removal in these cases requires an initial dissociation reaction step into the water before reacting with the amine, which could explain why lower strength (large water content) solvent shows better removal rates. Salting out of the mercaptan salt or a mass transfer impact from the higher viscosity at higher strength could be potential explanations. Further investigation of this trend is required to draw valid conclusions.

**Other sulfur species.** Significantly fewer data points are available for heavier mercaptans and other sulfides. The percentage removal of these species in various amines is given in TABLE 2. More data for these species are required before any correlation is meaningful, or for conclusions to be drawn.

DMS was present in significant quantities in 9 of the 50 measured gas absorbers. In all instances, the gas in question was refinery fuel gas. No clear trends were

observed and the number of data points per amine type were very limited. The removal of DMS ranged from 0%–88% efficiency with inlet DMS in sour gas ranging from 33 ppmv–784 ppmv.

There was not a large amount of statistically significant data for MES. In one instance, two absorbers in series using

MEA with 38 and 35 trays, respectively, reduced the MES content from 87 ppmv to 73 ppmv, and then from 73 ppmv to 52 ppmv, respectively. This configuration is unusual and saw significant formation of DMDS (8 ppmv–89 ppmv) in the first 38-tray absorber—the science explaining this observation is not fully developed.

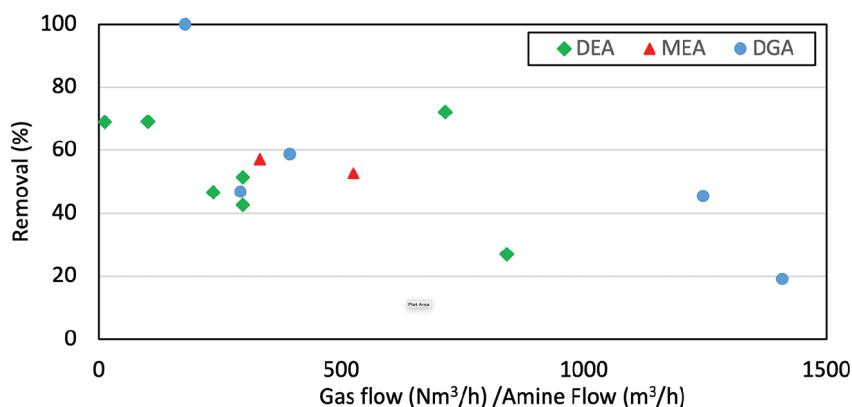


FIG. 5. Methyl mercaptan removal in primary and secondary amines vs. absorber V/L ratio for 14 absorbers.

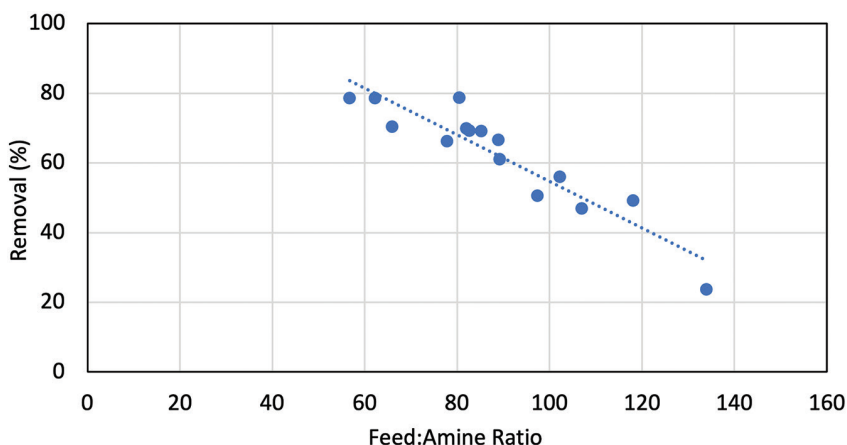


FIG. 6. Methyl mercaptan removal in DEA vs. absorber V/L ratio for absorber T2904 at PreemRaff Lysekil.

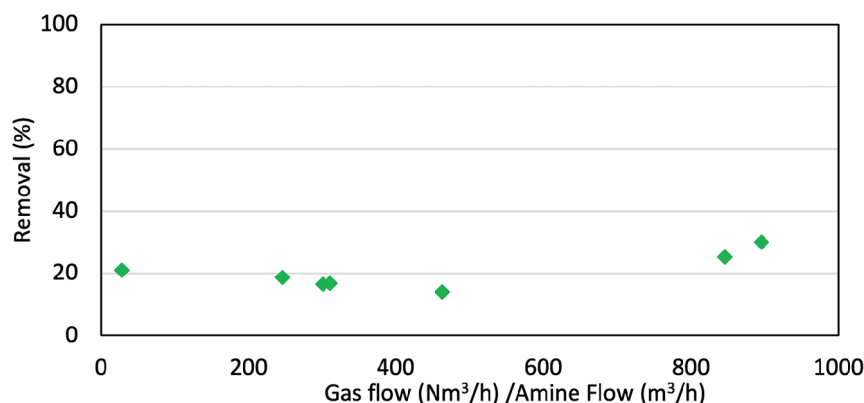


FIG. 7. Methyl mercaptan removal by MDEA vs. absorber V/L ratio for seven absorbers.

DMDS was (generally) not present in the gas inlet to the treaters. Two instances were found in addition to the situation mentioned above. In the first MDEA fuel gas absorber, operating at 6 barg, the DMDS concentration decreased from 18 ppmv to 8 ppmv across the treater. Secondly, in a DEA absorber operating at 6 barg, the inlet DMDS concentration decreased from 14 ppmv to 11 ppmv.

**Simulated vs. actual removal with DEA.** Three commercially available simulators were considered for their ability to predict organic sulfur removal from a fuel

gas by generic DEA solvent. Simulators 1 and 2 had  $R_1SH$ ,  $R_2SH$ ,  $R_3SH$ ,  $R_4SH$ , COS and DMS as available components, while Simulator 3 only had the capability to predict  $C_1SH$  and  $C_2SH$  removal and was therefore not included in this assessment.

The measured removal of the mercaptan species from a recent field test (not Preemraff Lysekil) was compared to the two model predictions (FIG. 10). From this and other industry experiences, it appears that current (2020) commercial simulators significantly underpredict the removal of organic sulfur species in generic amine systems.

**Onsite optimization at Preemraff Lysekil.** As part of the emissions minimization strategy at Preemraff Lysekil, an analytical test was conducted across the facility's treating system to identify sources of sulfur emissions. Onsite testing eliminated the TGTU, as it was working exceptionally well and no tail gas from the Claus plant was leaking into the stack. Further analysis of the main amine system traced the source of the emissions to organic sulfur species in the fuel gas. These species were mainly entering the system via a DEA fuel gas absorber, which was also treating vaporized LPG from a thermal cracking unit (visbreaker). During the testing, some variations were detected in the inlet composition and the feed gas flowrate. The bulk of the sulfur leaving this column with the treated fuel gas was in the form of methyl and ethyl mercaptan.

Follow-up test runs were arranged to determine if the organic sulfur species in the fuel gas and, therefore, the  $SO_2$  emissions from the plant, could be reduced by operational changes. Adjustments to column temperature and pressure did not show appreciable results: ranges were limited by hardware considerations. Adjustment of the upstream cut-points on the visbreaker unit did, however, have a significant impact and sent more mercaptans and DMS to the light naphtha fraction rather than to the fuel gas absorber. The light naphtha fraction is subsequently hydrotreated, effectively converting the mercaptans and DMS to  $H_2S$ , which can easily be absorbed in an amine treater.

The absorber was initially operating at low flood levels and, as such, did not have a high degree of contact between the amine solvent and the gas. The low contact was sufficient for the removal of  $H_2S$  and COS, but the removal of the mercaptans was not optimal. Once the amine circulation was increased, the methyl mercaptan removal by the DEA solution increased from 24% to 78% (see FIG. 6). For ethyl mercaptan, there was a step-change increase from 15% removal to 40%–60% removal as the amine flow rate was increased to the point where there was adequate contact (FIG. 11). From that point, at subsequent smaller gas-to-amine ratios, there is no obvious correlation to the removal of  $R_2SH$ .

By adjusting gas-to-amine solvent ratios, it was possible to increase the removal of the organic sulfur species from 21% to 71% of the inlet concentration.

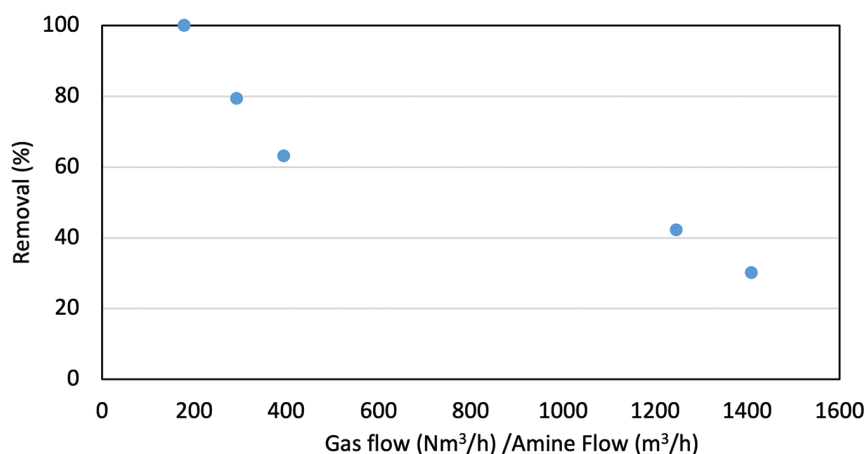


FIG. 8. Ethyl mercaptan removal in DGA vs. absorber V/L ratio for 5 absorbers.

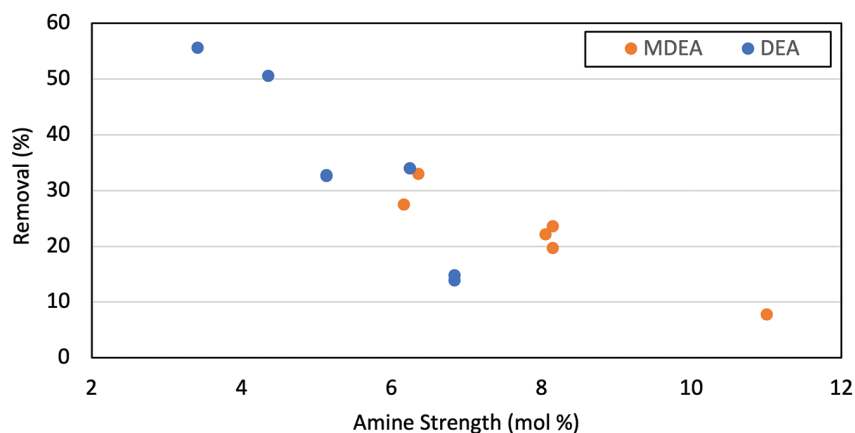


FIG. 9. Ethyl mercaptan removal in DEA and MDEA vs. solvent strength.

**TABLE 2.** Field measured removal percentage of  $C_3SH$ ,  $C_4SH$ ,  $C_5SH$  and DMS in various amines

	$C_3SH$ (# data points)	$C_4SH$ (# data points)	$C_5SH$ (# data points)	DMS (# data points)
MEA	39 (1)	45 (1)	–	35–67 (2)
DEA	30–79 (4)	34–83 (3)	26 (1)	22–68 (5)
MDEA	13–29 (3)	50 (1)	44 (1)	70–88 (2)

The adjustment of upstream cut-points increased this further—the net result is that the organic sulfur species in the treated gas were reduced by 94% after field optimizations.

At the end of the test run,  $\text{SO}_2$  emissions associated with this absorber declined by more than an order of magnitude. Determining the source of the  $\text{SO}_2$  emissions and then optimizing process conditions during a dedicated test run, with testing and analytical support, significantly decreased the already-low emissions from the facility.

**Takeaways.** Field data reveal that generic amines are capable of better organic sulfur removal than historical literature or commercial simulators now predict.

In one instance, DGA was able to achieve 100% removal of the COS,  $\text{CH}_4\text{S}$ ,  $\text{C}_2\text{H}_6\text{S}$  and  $\text{C}_3\text{H}_8\text{S}$ , albeit at low gas-to-solvent rates, which is not beneficial for plant CAPEX and OPEX. Removal of  $\text{CH}_4\text{S}$  and  $\text{C}_2\text{H}_6\text{S}$  by DGA correlated with gas-to-solvent ratios, with lower ratios showing higher rates of removal. Other operating parameters investigated did not appear to have a major impact for DGA.

DEA data shows a correlation between COS and  $\text{CH}_4\text{S}$  removal and gas-to-solvent ratio, as well as an unusual correlation between  $\text{C}_2\text{H}_6\text{S}$  removal and lower solvent strength. Removal of up to 100% of COS, 80%  $\text{CH}_4\text{S}$  and 60%  $\text{C}_2\text{H}_6\text{S}$  was observed on some systems.

Absorption of COS by MDEA appeared to be linked to the temperature bulge within the absorber, with 80% absorption of COS by MDEA being the maximum observed. MDEA showed low absorption of methyl mercaptan (20%–30%) with no obvious correlation between the amount of absorption and other process parameters.

For ethyl mercaptan removal, the data showed an interesting trend of better removal of ethyl mercaptan with declining amine strength for MDEA and DEA, which could potentially be explained by a reaction mechanism in which the ethyl mercaptan reacts with the water initially, or viscosity effects.

For propyl, butyl and pentyl mercaptan, removal in the range of 20%–80% was observed in the field results, but there were insufficient data to establish links with process parameters or to draw significant conclusions. The removal of

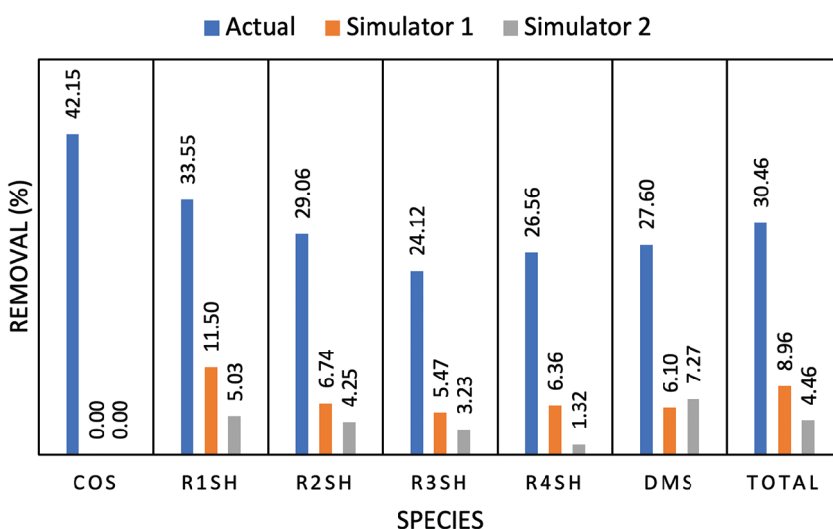


FIG. 10. Simulated vs. actual organic sulfur removal in a DEA fuel gas absorber.

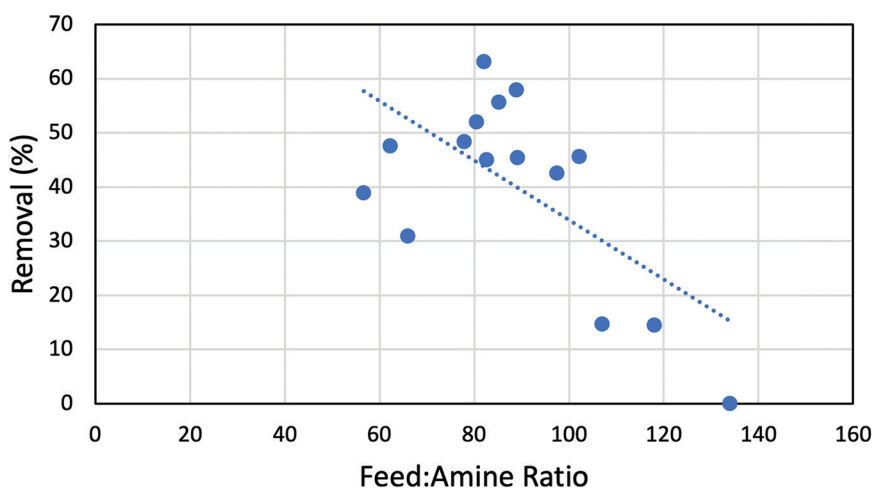


FIG. 11. Ethyl mercaptan removal in T2904 at Preemraff Lysekil.

DMS ranged from 22%–88%, with MEA/DEA/MDEA capable of removing 70% under certain process conditions.

In some instances, significant reductions in organic sulfur in treated gas are possible by optimizing process conditions. This is best done through onsite analytical testing, as both the fundamental understanding of the behavior of organic sulfur species and the simulation of this behavior need improvement.

Further research is needed to improve the industry's ability to predict (and hence optimize) organic sulfur species removal in amine systems. Specifically, improvement in simulator prediction capabilities is required. This will potentially require the generation of new or better experimental data for the solubility and absorption of organic sulfur species in

amine systems on which simulator predictions are based. Also of interest is the formation chemistry of some organic sulfur species in amine systems (e.g., mercaptan formation from sour amine in the presence of methanol) and potential routes for DMDS formation. **HP**

#### ACKNOWLEDGEMENT

The authors would like to thank Preem AB for granting permission to publish data from its Lysekil facility.

#### NOTES

<sup>a</sup> Tedlar® bags

<sup>b</sup> Sulfinert® cylinders

<sup>c</sup> Agilent 6890 or 7890 gas chromatographs

<sup>d</sup> Agilent GasPro columns

#### LITERATURE CITED

Complete literature cited available online at [www.HydrocarbonProcessing.com](http://www.HydrocarbonProcessing.com).



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## New state-of-the-art in sulfur recovery?—Part 1

It is widely accepted that state-of-the-art sulfur recovery technologies utilize the modified Claus process as well as some extension technology on the tail gas. To achieve the highest sulfur recovery, the extension technology converts all tail gas sulfur species to hydrogen sulfide ( $H_2S$ ) by hydrogenation and hydrolysis, which is subsequently captured in an amine absorber and recycled to the Claus thermal reactor. The industry has developed amine solvents of increased  $H_2S$  selectivity, with the most selective often regarded as the best available technology.

One of the more interesting challenges to the tail gas treatment technology described above is the direct conversion to sulfuric acid—after all, that is the destination of much of the recovered sulfur. However, the logistics of that approach are complex, primarily with respect to local sulfuric acid demand. Technically, conversion to sulfuric acid can provide better economics and decreased environmental impact, if there are no transportation restrictions.

Worley Comprimo and Topsoe have developed a proprietary sulfur recovery

process<sup>a</sup> based on proven technology, whereby sulfuric acid produced in a wet gas sulfuric acid (WSA) tail gas treating unit (TGTU) is recycled back to the Claus thermal reactor. With fewer equipment items and demonstrable high reliability, coupled with an energy balance benefit evidenced by operating plants and studies, the new flow scheme challenges for the position of best available technology.

A series of three articles presented here and in two subsequent issues of *Hydrocarbon Processing* cover all aspects of the technology. The first covers the technological aspects and development, while the second and third articles cover environmental and economic aspects, respectively. Case studies covering a range of Claus plant acid gas feed streams are used for the economic comparisons.

By way of introduction to the technology, six key points of the sulfur recovery process<sup>a</sup> configuration should be stated:

- The WSA TGTU is robust against variations in Claus tail gas composition and can process ammonia containing sour water stripper (SWS) offgases, which can

be routed directly to the WSA unit.

- The equipment count is lower than that in a Claus/hydrogenation/hydrolysis/amine configuration, and the Claus plant equipment is smaller.
- The overall sulfur recovery is equivalent to that achieved in a Claus/hydrogenation/hydrolysis/amine configuration, with sulfur dioxide ( $SO_2$ ) emissions of  $150 \text{ mg/Nm}^3$ , or whatever is required at the location of the plant.
- Thermal efficiency is high with high-pressure (HP) steam exported from the WSA, and little cooling is needed.
- There are no waste streams.
- No chemicals are required.

While the combined technology is new, its components are well-established in industry: the Claus process, the WSA process and the handling of sulfuric acid.

Current industry trends include:

- Sulfur continues to be a significant byproduct from oil and gas upgrading
- Most new oil and gas fields are sour
- Tightening of sulfur emissions standards will continue
- Operators are looking to reduce their carbon footprint
- Operators are striving to meet emissions standards at minimum CAPEX and OPEX with optimized technology.

Although sulfur is a product and continues to be a significant byproduct from oil and gas upgrading in both refining, gas plants and various other processes, it is—for many in the oil and gas industry—often regarded as a waste product. This is not going to change fundamen-

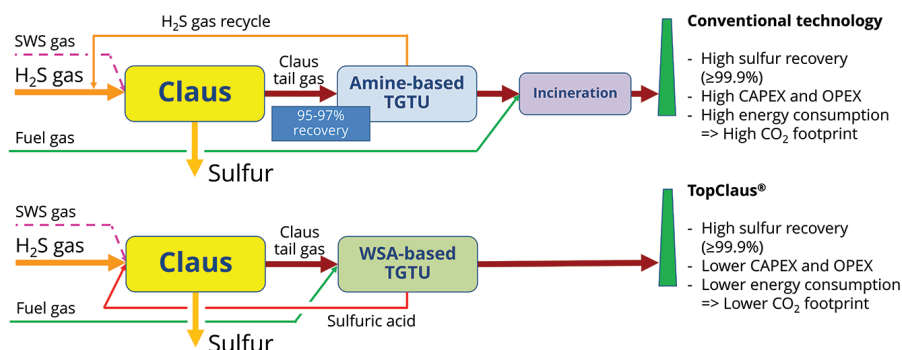


FIG. 1. Claus tail gas treatment options.

tally as the world continues to transition to renewable fuels that also contain sulfur compounds that must be removed.

Most new oil and gas field discoveries today are sour and do require a certain amount of cleaning up as part of bringing the products to market. Global sulfur emissions standards, for both hydrocarbon products and emissions from refineries, gas plants and production facilities, are continuing to tighten. Over the past few decades, this has been evident with some facilities upgrading Claus units and now investigating further emissions reduction with hydrogenation and amine-based TGTUs. Additionally, operators are looking to reduce their carbon footprint to reflect the exponential increase in carbon dioxide ( $\text{CO}_2$ ) footprint as  $\text{SO}_2$  emissions are reduced close to zero in those types of TGTUs.

### Claus process with conventional TGT.

The Claus process with conventional tail gas treatment, shown in FIG. 1, typically comprises a two-stage catalytic Claus plant combined with a hydrogenation/hydrolysis and amine-based TGTU, sometimes referred to as a BSR/amine plant, or SCOT plant. The offgases that contain small amounts of  $\text{H}_2\text{S}$  and COS are typically converted to  $\text{SO}_2$  in a thermal oxidizer before venting to atmosphere.

Sulfur recoveries > 99.9% are possible but at a relatively high CAPEX and OPEX. It is in the last few percentage points where costs escalate; the process is energy-intensive and this is reflected in carbon footprint.

The conventional hydrogenation and amine-based TGT was first patented by the Ralph M Parsons Co. in 1971, with other companies quickly following suit. Incremental improvements have been made throughout the years, but the process largely remains the same. Improvements with the amines used are related to increased  $\text{H}_2\text{S}$  selectivity (often using proprietary amines), but the process is largely the same. Regardless, amine regeneration is energy intensive.

Alternatives can offer lower CAPEX and OPEX. One example would be Comprimo's Claus tail gas direct oxidation technology<sup>b</sup> that, when coupled with caustic scrubbing, achieves very low sulfur emissions. CAPEX is lower, but there is an additional waste stream (spent caustic) that has associated disposal costs. However, this configuration is only appli-

cable to relatively low-sulfur plant capacities, and typically (but not exclusively) to refinery plants with sulfur capacities < 300 tpd sulfur. Topsoe's WSA process also offers an alternative TGT technology; to date, some 165 units have been licensed.

The new sulfur recovery process<sup>a</sup> technology (FIG. 2), using a WSA TGTU with acid recycling, reduces energy intensity but still maintains the sulfur recovery of > 99.9%. Equipment count, CAPEX and carbon footprint are all reduced. The product is still sulfur, but

with enhanced operational benefits.

Enhanced sulfur recovery of > 99.95% is also achievable by the WSA TGTU with double condensation. This is a refined solution that consumes no chemicals and produces no effluents. Other alternatives exist, such as tail gas scrubbing using chemicals like hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) or sodium hydroxide ( $\text{NaOH}$ ), which are cheaper than double condensation but have chemical consumption and, in the case of  $\text{NaOH}$ , an effluent stream to be dealt with.

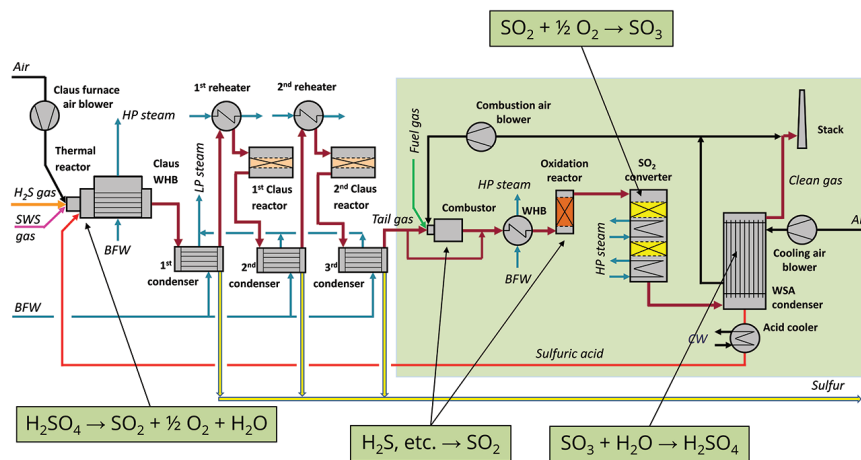


FIG. 2. A simplified process flow diagram of the new sulfur recovery process<sup>a</sup>.

### $\text{H}_2\text{SO}_4$ (droplet)

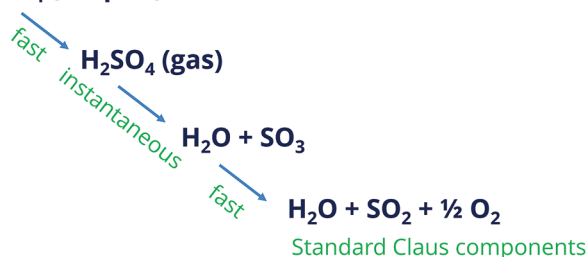


FIG. 3. Claus reaction furnace chemistry: the fate of recycled  $\text{H}_2\text{SO}_4$ . Source: Alberta Sulphur Research Ltd. (ASRL) and HEC Technologies.

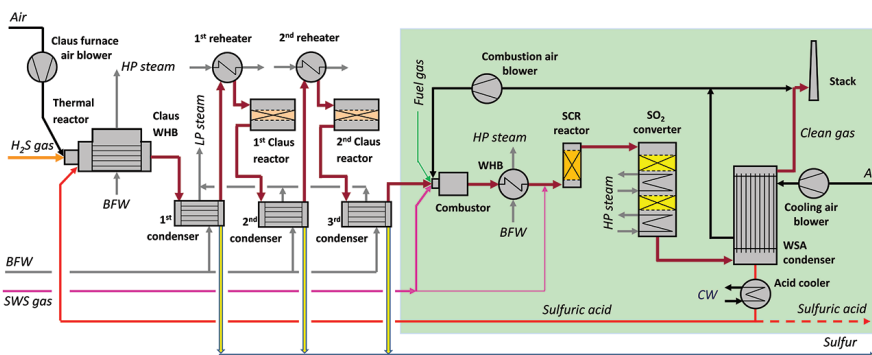


FIG. 4. The proprietary sulfur recovery process<sup>a</sup> with SWS gas to the WSA section.

Sulfuric acid is recycled to the Claus furnace and the key chemical reactions are included here.

**The consideration of dilution gas is worth noting.** In the overall Claus reaction, there are 12 moles of dilution gas for every four sulfur atoms produced. Using pure oxygen rather than air, the nitrogen is removed, leaving just four moles of dilution gas. Recycle acid is an excellent oxygen carrier and leads to only 4.4 moles of dilution gas, facilitating the reduction of air demand to ~20%. Another comparison with a conventional TGTU is that there is no CO<sub>2</sub> in the recycle stream to the furnace. These factors contribute to a capacity increase in the Claus section.

Key questions arising from this are how quickly liquid acid would be vaporized; how quickly the gas would disassociate; and how quickly the standard Claus components would be formed. These questions were investigated independently by Alberta Sulfur Research Ltd. (ASRL) and HEC Technologies and answered, as shown in **FIG. 3**.

Particularly for refinery applications, an alternative for processing SWS offgas with the new sulfur recovery process<sup>a</sup> becomes apparent. Traditionally, these gases—which contain ammonia, hydrogen sulfide and water vapor—are routed to the front section of a two-stage Claus thermal reactor operating at 1,250°C to ensure the complete destruction of ammonia. Inadequate ammonia destruction (e.g., in a single combustion zone thermal reactor operating at ~1,000°C) can lead to ammonium salt deposition at the final condenser, especially when cooled using a 1-barg closed-loop cooling arrangement.

The new sulfur recovery process<sup>a</sup> configuration allows routing of the SWS gases directly to the combustor in the WSA section, as shown in **FIG. 4**, simplifying the Claus section and avoiding the potential deposition problem. The SWS gas is burned in the combustor of the WSA section with excess air. This leads unavoidably to some formation of nitrogen oxides (NO<sub>x</sub>), which are removed again in the SCR reactor located after the waste heat boiler. A small fraction of the SWS gas is added to the combustor effluent after the waste heat boiler to provide enough ammonia to react with the formed NO<sub>x</sub> over the catalyst installed in the SCR reactor. The results of the reaction are nitrogen and water vapor.

The feasibility of this concept, however, must be evaluated in each individual case and depends on several factors, such as:

- The ratio between amine acid gas (i.e., with no ammonia present) and SWS gas flows
- The required overall SRE
- The possibility of exporting a certain amount of sulfuric acid as a separate product.

Often, it will be necessary to have the SWS gas processed in the Claus section.

**Takeaway.** The new sulfur recovery process<sup>a</sup> achieves a sulfur recovery equivalent to the conventional design, is a simpler process with fewer parameters to control, and the economic benefits are substantial. The Claus unit itself will be smaller due to the recycle and oxygen carrying capacity of the acid.

Additional flexibility can be provided by producing a small sulfuric acid stream, which could be useful in a refinery application, though special circumstances would be required to progress this route. Maintaining a single product stream is going to be preferable in most applications.

Brownfield applications (i.e., revamps) provide unique opportunities, with perhaps limited space, a need for increased capacity, and a requirement to meet increasingly tight emissions specifications. The WSA section can be constructed while the Claus unit is in operation, so it provides minimum shutdown time, minimum personnel onsite and simultaneous operations (SIMOPS) advantages, in general.

The application to natural gas plant SRUs affords some enhanced benefits for the sulfur recovery process<sup>a</sup>, including:

- Significant CO<sub>2</sub> in the feed reduces the thermal reactor temperature and increases the size of the conventional TGTU
- CO<sub>2</sub> co-absorbed in amine-based TGTUs is recycled to the inlet of Claus unit
- TGTU amine requires leaner loading to allow CO<sub>2</sub> “slip”
- All CO<sub>2</sub> passes through to the stack
- Smaller recycle = smaller SRU
- Simple, robust and efficient
- Sulfur recovery of > 99.9% with all sulfur compounds converted into elemental sulfur
- Flexibility in production

- All product is elemental sulfur
- Reduced Claus unit size due to sulfuric acid recycle, providing a degree of oxygen enrichment
- No waste streams
- Feasible solution for both greenfield and brownfield applications
- High thermal efficiency with HP steam export
- Integrated efficient features of WSA with the sulfur-producing Claus process
- Based on proven technologies with integration demonstrated by ASRL.

Parts 2 and 3 of this article will appear in subsequent issues of *Hydrocarbon Processing* and will cover environmental and economic aspects, respectively. **HP**

## NOTES

<sup>a</sup> TopClaus®

<sup>b</sup> Comprimo's SuperClaus®



**JON LEWIS** leads UK Operations for Comprimo, part of the Worley group, after serving as Global Director for gas processing. Lewis's responsibilities span consultancy, project delivery, client support and business development. He has

extensive conceptual and detailed engineering experience and has held various roles associated with gas processing terminals, offshore platforms and refineries in his 29-yr career with the company, as well as managing the London Process Department from 2004–2011. Lewis graduated with an MS degree in advanced chemical engineering from the University of Manchester (UMIST) in the UK, is a Chartered Engineer and Fellow of the Institute of Chemical Engineers (FICHEME), and has published articles and presented at international conferences.



After graduation as chemical engineer, **FRANDS E. JENSEN** has been working for Topsoe since 1979 in various marketing and sales positions and has been dealing with most of the technologies offered by Topsoe. Since 2003, Jensen has concentrated on the WSA, SNOX™ and TopClaus® technologies applied for sulfur removal from offgases as Senior Sales Manager.



**HESBON NJUGUNA** is a Principal Process Engineer at Comprimo, part of the Worley group, and has extensive experience working in the design of sulfur recovery plants constituting the Claus process, SWS, amine regeneration and

TGTUs throughout his 15-yr career with the company. Njuguna has been heavily involved in the early development of the TopClaus® technology. He graduated with an honors degree in chemical engineering from the University of Nottingham in the UK and earned an MS degree in forensic engineering and science from Cranfield University in the UK. Njuguna is a Chartered Engineer and Member of the Institute of Chemical Engineers (MICHEME).



## The heavy toll on sulfur blocks

The tightening of environmental norms and emissions specifications provides additional challenges to refining. The International Maritime Organization (IMO) 2020 sulfur specifications of bunker fuel oil from 3.5 wt% to 0.5 wt% have made the refining industry reconsider how heavy fractions of crude oil are handled. Typically, the vacuum residue found an easy way out of the refinery through the bunker fuel oil route, and sulfur specifications were met relatively easily by blending an adequate amount of cutter stock.

Generating low-sulfur fuel oil for the shipping industry to meet the sulfur specifications would induce the addition of a residue hydrotreater in the refinery to remove sulfurous compounds from the bunker oil. However, this is generally not the most favored route since, in most cases, it becomes economically nonviable to invest in an expensive hydroprocessing unit for the vacuum residue to generate a nonvaluable, low-sulfur bunker oil product.

Perhaps, a more lucrative opportunity is to opt for a residue upgrade project, where the vacuum residue is converted into more lucrative light and middle distillates. Residue upgrade constitutes any processing scheme that converts the heavy vacuum residue fraction partially or completely into lighter products. Depending on the severity of the operation, the conversion may be considered mild, where only a small fraction gets converted, or severe, where most of the residue is targeted to generate light and middle distillate products. Various process technologies may be applied to convert the heavy residue to lighter products. **TABLE 1** provides a brief overview of the three significant types of residue upgradation processes implemented in modern refineries.

Whatever residue conversion process is implemented will impact the refinery's overall sulfur balance. The sulfur load

increase on the refinery sulfur block depends on the crude diet and the type of residue upgradation process implemented. The most striking feature in a residue upgradation process is the out-of-proportion increase of ammonia ( $\text{NH}_3$ ) feed to the sulfur block.

The explanation for this phenomenon— $\text{NH}_3$  generation increasing much more than hydrogen sulfide ( $\text{H}_2\text{S}$ )—is related to the fact that nitrogen concentrates more than sulfur in the heaviest fractions of crude. Consequently, in a residue upgrade project, the impact on the sulfur block is further complicated as the increase of sulfur load is always complemented by a multifold increase in  $\text{NH}_3$  feed.  $\text{NH}_3$  coprocessing in the sulfur block presents its challenges, as this article will show with two specific case studies.

The two case studies presented are related to two separate residue upgrade projects, each showcasing its huge impact on the sulfur block design, and how smart and unique design methods may be implemented on the overall sulfur block.

### CASE 1: DELAYED COKER WITH SRU REVAMP

The first case study is a 100,000-bpd hydroskimming refinery in a coastal location that processes a relatively high-sulfur Russian crude (> 2 wt% sulfur content).

The refinery is equipped with hydrotreaters for naphtha, kero and diesel. Desulfurized naphtha is further processed to boost the octane number, resulting in isomerate and reformat sold as gasoline blendstocks, whereas the desulfurized kero and diesel are sold as blend components for automotive diesel. The vacuum gasoil (VGO) is exported to another refinery to be converted into transportation fuels in the hydrocracker or fluid catalytic cracker.

The vacuum residue was originally processed in a visbreaker before being sold as marine fuel oil. The visbreaking operation reduced the cutter stock necessary to blend into the fuel oil to meet viscosity requirements while also converting a small fraction of the vacuum residue into naphtha and middle distillate. High-sulfur marine fuel oil production amounts to roughly 20% of the crude intake.

In view of IMO 2020, the strategy selected by this refinery was to implement a delayed coker and shutdown the existing visbreaker (**FIG. 1**). This option eliminates producing marine fuel oil altogether, substituting it with much smaller exports of petroleum coke. The naphtha and middle distillate (light coker gasoil) streams produced by the delayed coker could be processed in existing naphtha and diesel hydrotreating units (with limited revamp modifications) since these units were al-

**TABLE 1.** Comparison of residue conversion process

	Non-catalytic (coker)	Catalytic (coker)	Catalytic with hydrogen (resid hydrocracker)
Process simplicity	Highest	Mid	Lowest
Operational flexibility	Lowest	Mid	Highest
Comparative cost	Lowest	Mid	Highest
Product quality	Lowest	Mid	Highest
Extent of residue conversion	Lowest	Mid	Highest
Coke formation	Highest	Mid	Lowest
Other challenges	Coke disposal	Heavy residue	Hydrogen requirement



ready handling the visbreaker naphtha and middle distillates.

Coker liquified petroleum gas can also be treated in existing installations. The heavy coker gasoil stream—which, as a thermally cracked material, is high in sulfur and nitrogen as well as unstable for transportation and storage—was to be processed in a new dedicated hydrotreater to produce a VGO boiling stable range material (so it can be transported) as well as low sulfur and nitrogen, making it easy to sell to third parties.

The project had a large impact on the overall sulfur block of the refinery. Sulfur production increased from 45 tpd to almost 100 tpd. Increasing  $H_2S$  production and sulfur recovery required a new amine regeneration system to supplement the existing system.

The substantial increase in sour water production required adding a new sour water stripper (SWS), as the existing SWS could not accommodate the future flow-rate. An important side benefit of having

two distinct units is that it enabled the segregation of sour waters in phenolic and non-phenolic streams (FIG. 2). The non-phenolic sour water originating from hydrotreaters, which contains no other impurities besides dissolved  $NH_3$  and  $H_2S$ , could be now advantageously re-used as make-up water in the delayed coker or make-up wash water in hydrotreaters.

The sour water produced by the delayed coker, which contains phenolic impurities and dissolved  $NH_3$  and  $H_2S$ , could be entirely used as make-up water to the crude desalter. This minimized the rundown of phenol to the wastewater treatment plant (where phenol is difficult to remove), as the phenol is largely re-extracted into the crude and subsequently decomposed in the hydrotreaters.

Additional complexities accompanied the increase in sulfur load. The  $H_2S$  to be processed in the sulfur recovery unit (SRU) increased more than two-fold, and the amount of  $NH_3$  to be processed increased by a factor of eight. This represented an additional extra hydraulic load on the SRU, resulting from the  $H_2S$  increase. Consequently, the gas throughput of the SRU increased by about three-fold in total.

The SRUs had similar capacities (about 50 tpd). One unit acted as a standby for the other in the existing refinery operating plan. Both units (A and B) were equipped with selective oxidation-type technology, enabling recovery efficiencies greater than 99%. Only Unit B was designed to co-process SWS gas. Both SRUs were equipped with oxygen enrichment and low-cost oxygen readily available by pipeline from an industrial gas supplier in the vicinity.

An assessment of the future loads of amine acid gas and SWS gas showed that the two existing SRUs could handle the future loads, provided that:

- Both SRUs would always be operated (no stand-by capacity).
- Both SRUs would always use oxygen enrichment.
- Unit A would be revamped to handle SWS gas and amine acid gas, necessitating a new knock-out (KO) drum with piping and instrument modifications. A new combustion chamber in the Claus furnace was not deemed required, despite a somewhat low residence time, since the operating temperature was always sufficiently high due to the use of oxygen enrichment, ensuring good  $NH_3$  destruction.
- Unit A would be revamped with deeper sulfur seals so it could be operated at higher pressure resulting from higher flowrates, taking advantage of spare differential pressure in the existing main airblower.
- Unit B, although already able to handle SWS gas, required limited revamp measures on the SWS gas KO drum and piping, enabling it to handle more SWS gas.

The requirement to always use both SRUs was not a comfortable scenario as it would result in acid gas flaring whenever one SRU tripped. The relevant authorities only accepted this simultaneous and continuous operation of both SRUs at the future higher-sulfur load in case the normal sulfur dioxide ( $SO_2$ ) emissions would be reduced.

A caustic-based absorption system was selected to achieve this requirement at the

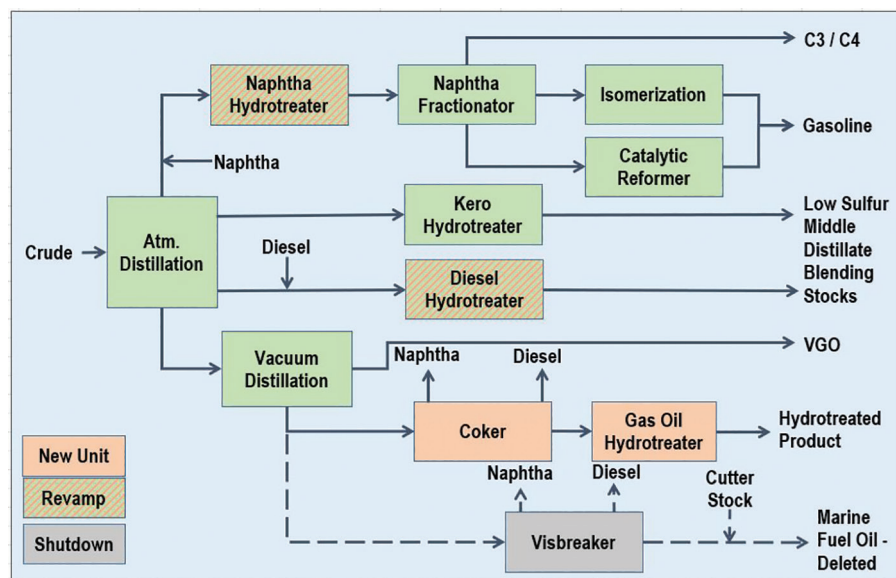


FIG. 1. Overall refinery block flow diagram.

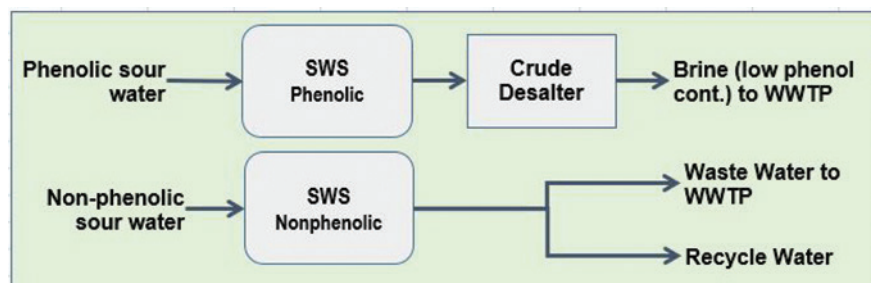


FIG. 2. Sour water segregation (SWS).

lowest possible cost (FIG. 3), treating the combined thermal oxidizer flue gas from both SRUs. Caustic-based absorption systems are a low-capital-cost option to eliminate SO<sub>2</sub> emissions in a simple configuration. This option was best suited for this case for the following reasons:

- Caustic consumption would be limited due to the high recovery efficiency (Note: at 99.5% recovery efficiency, caustic consumption to achieve full SO<sub>2</sub> removal is eight times lower at 97%).
- The inevitable high-salt content effluent, containing all absorbed SO<sub>2</sub> in the form of dissolved sodium sulfate salt, could be disposed of without major problems because this refinery was in a coastal location.
- Both Units A and B were equipped with forced-draft thermal oxidizers, facilitating the insertion of the caustic-based absorption system downstream of the oxidizers.

The cost of the described revamping measures was substantially lower than the alternative of adding a new SRU train to meet the required capacity and operational flexibility.

## CASE 2: RESIDUE HYDROCRACKER WITH TWO OPERATING CASES

The second case study presented here is regarding a refinery revamp, which included the addition of an ebullated bed hydrocracker to convert the vacuum residue to light and middle distillates. The project's unique feature was that the refinery was designed for two extremely heavy crude diets: Crude A was very high in sulfur impurities, and Crude B was much sweeter but had much more nitrogenous impurities.

This unique combination of crude diet generated two very different sulfur and nitrogen balances for the refinery. For Crude A, the sulfur load to the sulfur block was highest, while for Crude B, the sulfur load was considerably lower but the NH<sub>3</sub> load was much higher due to the high nitrogen content. The NH<sub>3</sub> load for Crude B was so high compared to the total H<sub>2</sub>S content in the amine acid gas and SWS gas that it was becoming challenging to achieve a high enough furnace temperature for complete NH<sub>3</sub> destruction in the Claus furnace.

NH<sub>3</sub> destruction in the Claus furnace is ensured when the furnace temperature

is kept high enough, ideally > 1,250°C at all operating conditions. The following options are available for increasing the furnace temperatures:

- **Maximizing the preheat:** Preheat all possible feed streams to the Claus furnace (amine acid gas, SWS gas and air). This is the simplest approach but is limited by the extent of preheating that may be achieved. Typically, the high-pressure steam generated from the waste heat boilers is used as the heating medium. The steam generated from the waste heat boilers is around 45 barg, so the maximum preheat temperatures that may be achieved for the feed streams would be limited to 240°C or less.
- **Oxygen enrichment:** Using oxygen enrichment significantly improves the furnace temperatures, as the inert nitrogen component of air is partially eliminated. The temperatures from the modified Claus reaction (the sulfur forming reaction) achieves a higher furnace temperature with a richer (oxygen) airflow. Low-level oxygen enrichment (up to 28 vol% of oxygen in the air/oxygen mixed feed to the furnace) may easily be applied with no major changes in furnace design, while mid-level oxygen enrichment (up to 45 vol% oxygen) required design updates on the Claus furnace and burner, as the burner would need an independent oxygen lance. Further oxygen enrichment may also be applied for extreme feed gas compositions (very lean concerning H<sub>2</sub>S content).
- **Fuel gas co-firing:** Another method to increase the furnace

temperature is to inject small amounts of fuel gas in the Claus furnace; the energy from burning the fuel gas would help increase the furnace temperatures. Typically, fuel gas co-firing is not recommended continuously and should be limited to intermittent usages for upset or abnormal feed gas compositions. Natural gas or equivalent quality gas should be fired in the Claus furnace, limiting the ingress of heavy hydrocarbons. However, the probability of soot formation while burning the hydrocarbons in the fuel gas can never be ruled out, as the furnace firing conditions are reduced at all normal operating conditions.

- **Two-zone furnace design:** Another unique way of managing the furnace temperatures for NH<sub>3</sub> destruction is to design the Claus furnace as a two-zone furnace, where some portion of the H<sub>2</sub>S-rich amine acid gas is bypassed and sent to the back end or the second zone of the furnace. The front zone thus burns with additional air, which helps it achieve a higher flame temperature. When the gas mixture reaches the second zone, the final temperature would be defined by the thermodynamic equilibrium for the modified Claus reaction.

Another alternative, also implemented in refineries to manage NH<sub>3</sub> in the SRU feed, is to utilize a two-stage SWS to separate the H<sub>2</sub>S-rich gas and NH<sub>3</sub>-rich gas. The NH<sub>3</sub> gas can then be combusted directly in the incinerator or even used as NH<sub>3</sub> for other uses, while the H<sub>2</sub>S-rich gas stream is fed into the Claus section for sulfur recovery. For the case study scenario, since the variation of the sulfur and nitrogen content

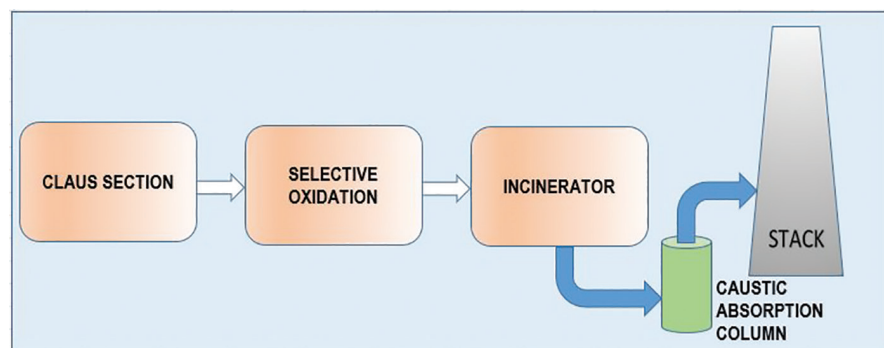


FIG. 3. Emissions management with caustic absorption.

in the two crude cases (Crudes A and B, as shown in **TABLE 2**) were so widespread, a two-stage SWS was implemented, which would generate two separate products from the SWS to be routed to the SRU—namely the H<sub>2</sub>S-rich gas stream, and the NH<sub>3</sub> gas stream with practically no H<sub>2</sub>S while running on Crude B.

The two-stage SWS design, as shown in **FIG. 4**, takes advantage of the different solubilities and affinities towards water for the two components: H<sub>2</sub>S and NH<sub>3</sub>. The H<sub>2</sub>S solubility in water is comparatively less when compared to NH<sub>3</sub>. The first column (H<sub>2</sub>S stripper) operated at a higher pressure, and almost the entire H<sub>2</sub>S load would be dissolved, leaving the NH<sub>3</sub> in the water phase to the second column

(NH<sub>3</sub> stripper). This requires operation at a much lower pressure to enable the NH<sub>3</sub> to be released from the aqueous phase.

As shown in **FIG. 4**, an additional H<sub>2</sub>S scrubber column may also be included in the design to ensure that the H<sub>2</sub>S slip in the NH<sub>3</sub>-rich gas stream is limited, mainly to limit the sulfur oxide emissions issues in the downstream SRU incinerator, as has been described in the SRU design aspects.

The design of the downstream SRU was also implemented to manage the H<sub>2</sub>S- and NH<sub>3</sub>-rich streams to complement the two-SWS design. The H<sub>2</sub>S-rich stream is routed in the front-end section or the Claus section of the SRU for sulfur recovery, whereas the NH<sub>3</sub>-rich stream is routed to the back end of the unit, to the

thermal incinerator, where it is burned off and released to the atmosphere. The split stream of NH<sub>3</sub>-rich gas is routed to the catalytic converter to manage the nitrogen oxide emissions limits (**FIG. 5**).

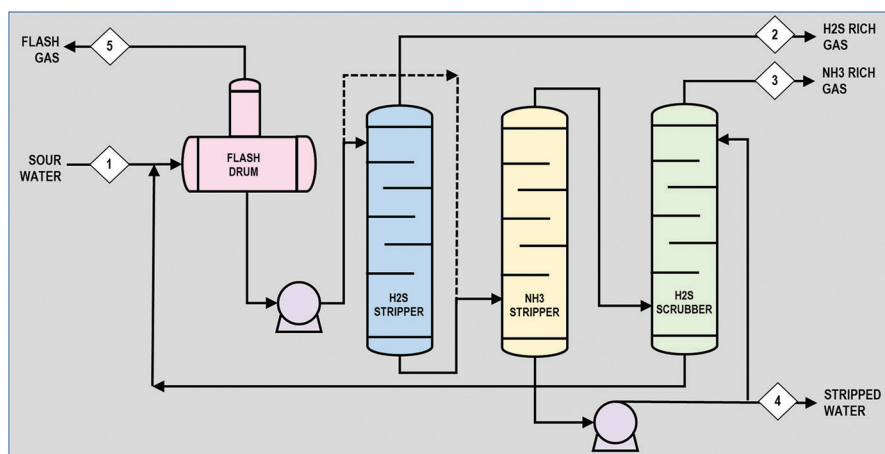
This design allowed the refinery operation to manage the two operating cases with Crudes A and B. As indicated previously, the two-stage SWS and the SRU operation to manage the high NH<sub>3</sub> are applicable for Crude B of the high nitrogen-containing crude.

However, when the refinery operates with Crude A, the two-stage SWS would operate as a normal single-stage SWS, whereby the first stage stripping section (H<sub>2</sub>S stripper) would be bypassed, as indicated by dotted lines in **FIGS. 4** and **5**. In this operating condition, there would be only a single SWS-rich gas sent to the SRU. The SRU operates in its normal mode, processing the amine acid and the SWS gas, as the total NH<sub>3</sub> in the SRU feed, for this case, is in the manageable range for the standard Claus furnace arrangement.

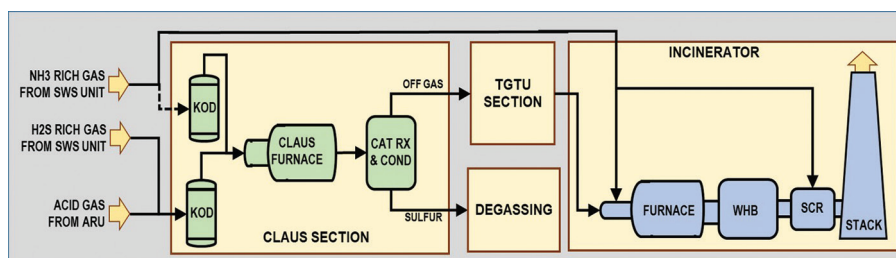
**Takeaway.** With the application for residue upgrade projects in refineries, there is an inherent increase in the sulfur load in addition to an out-of-proportion increase of NH<sub>3</sub> load on the existing sulfur blocks. Depending on the nature of the applied residue upgrade technology, the refinery configuration and the crude diet, the impact on the sulfur block also varies widely. Existing sulfur blocks need a significant overhaul or new SRU to meet the additional loads. The varying operating parameters of the revamped refinery add additional complexity to the sulfur block design. Therefore, proper design of the sulfur block to meet the post-revamp requirements for all operating scenarios is of utmost importance and relevance, not only to achieve a techno-economical optimum refinery but also to overcome the environmental requirements of the project. **HP**

**TABLE 2.** SRU feed gas compositions

Parameter	Crude A		Crude B	
	Acid gas from amine regeneration unit (ARU)	Acid gas from SWS	Acid gas from ARU	Acid gas from SWS
Flow, kg/hr	6,200	1,090	970	1,350
H <sub>2</sub> S, mol	171.3	17.7	24.5	24.4
NH <sub>3</sub> , mol	0.1	17.4	0	27.6
Capacity, tpd of sulfur	145		38	
(NH <sub>3</sub> ) : (NH <sub>3</sub> + H <sub>2</sub> S)	8.50%		36%	



**FIG. 4.** Simplified scheme for a two-stage SWS unit.



**FIG. 5.** SRU design for the management of sour gases from SWS.

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## A novel deep catalytic cracking technology for residue-to-chemicals processes

Over the past two decades, annual global demands for refined products and basic petrochemicals have increased by approximately 1.3% and 3.5%, respectively. Many refiners around the world are focusing on improving their operations to co-produce petrochemical feedstocks as demand for refined products is forecast to decline. The production of basic petrochemicals accounted for 14 MMbpd of global crude oil demand in 2018 and is forecast to increase to 20 MMbpd by 2050, accounting for approximately 50% of the expected growth in oil demand. In addition, global demand for ethylene and propylene is forecast to increase from 270 MMtpy in 2018 to 385 MMtpy in 2030.

Fluid catalytic cracking (FCC) has become the second major propylene production technology after steam cracking, showing high flexibility in feedstocks and product distribution. FCC units (FCCUs) typically use vacuum distillation products, namely vacuum gasoil (VGO) and vacuum residue as feedstocks. Deep catalytic cracking (DCC) is an FCC process that uses proprietary catalysts to selectively crack various heavy feedstocks to light olefins. The process was developed by the co-authors' company and has been commercially proven since 1990 through more than 10 installed units. The DCC process is like the traditional FCC process, with the modified reactor consisting of a riser and a fluidized dense bed. The dense bed at the

end of the riser results in longer residence times at high catalyst/oil ratios, favoring secondary cracking of primary intermediates, which is believed to increase propylene production at the expense of gasoline yield. It is noteworthy that DCC has poor adaptability to feedstocks. The density of feedstocks is generally not more than 0.92 g/cm<sup>3</sup>, and the hydrogen content is not less than 12.6 wt%. As the quality of the feedstocks tends to be heavier, the application of DCC technology is greatly limited.

**Analysis of the DCC reactor.** For a long time, research on the DCC reactor (FIG. 1) has been neglected. The proprietary catalyst—consisting primarily of ZSM-5—has a short residence time in the riser, which is insufficient to convert heavy oil to light olefins. Therefore, the combination of a riser and an additional fluidized dense bed is generally considered to be a good choice for DCC focused on enhancing olefin production. Nevertheless, this combination of reactors has several disadvantages, which are discussed below.

The regenerated catalysts are transported to the bottom of the riser for contact with feedstocks. The feedstock then undergoes evaporation and catalytic cracking. Since the riser operates in the dilute phase bed, not all feed molecules can effectively contact the catalysts. Those heavy oil molecules that are not in contact with the regenerated catalysts may under-

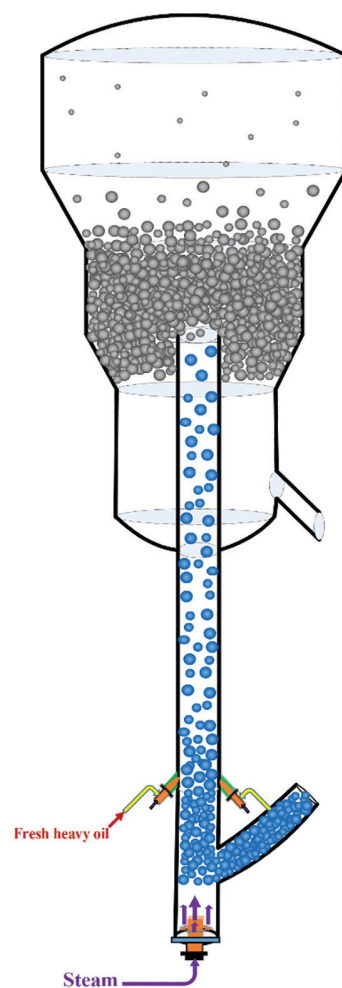


FIG. 1. The configuration of the DCC reactor, consisting of a riser and a fluidized dense bed.



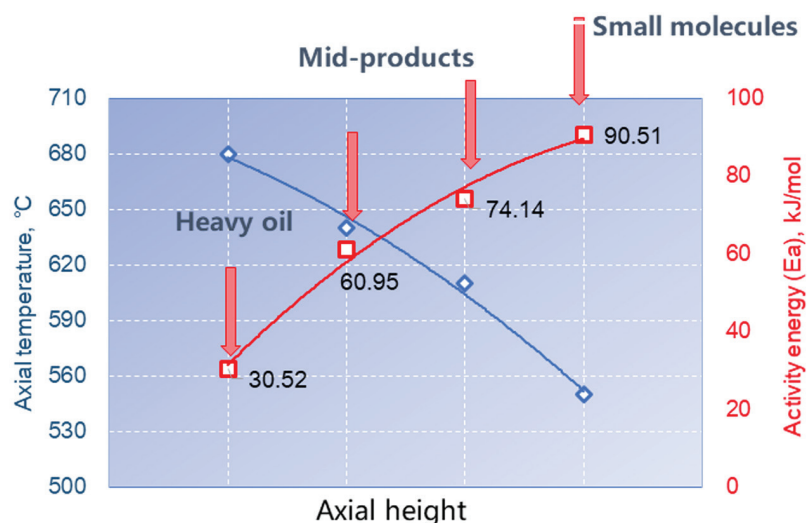


FIG. 2. Temperature profile and activation energy for producing propylene along the axis of the riser.

TABLE 1. Experimental results of DCC of inferior feedstocks in different reactors

Reactor	Riser	Riser + dense-phase bed	Dense- phase bed	Fast- fluidized bed	Specially configured fast-fluidized bed
Feedstock					
Density (20°C, kg × m <sup>-3</sup> )			934.2		
CCR			5.58		
Hydrogen content, wt%			12.15		
Catalysts			Customized catalyst		
Product distribution					
Ethylene, wt%	3.12	3.89	5.3	3.34	4.86
Propylene, wt%	10.93	12.67	14.74	12.42	16.63
Coke	7.14	11.23	12.24	9.5	10.24

go unwanted thermal cracking, producing byproducts (such as methane and coke) instead of propylene. When the catalysts enter the fluidized dense bed, some coke has accumulated on the surface or in the pores. Even operating in the dense bed, these partially deactivated catalysts are less capable of further cracking intermediates, such as gasoline to propylene, and may instead lead to more coke formation.

The temperature at the bottom of the riser must be controlled to suppress thermal cracking. The axial temperature drop along the riser can reach more than 50°C (122°F). However, the activation energy to produce propylene rises with the increasing cracking depth of the feedstock. Consequently, the temperature profile within the combined reactor of the DCC unit is inverse to the desired temperature profile for propylene production, as shown in FIG. 2.

DCC technology is more suitable for processing paraffin-based VGO. With the deterioration of crude oil worldwide, the availability of suitable feedstocks for DCC has gradually reduced. When processing inferior heavy oil, the yields of coke, light catalytic cycle oil, slurry and methane increase significantly. Therefore, new reactors for DCC must be developed to achieve better ethylene, propylene and gasoline yields, even with ultra-inferior feedstocks.

**DCC of inferior feedstock in different types of reactors.** To develop a new reactor suitable for DCC of inferior feedstocks, the catalytic cracking of an intermediate base hydrotreated residue was evaluated in different types of reactors. The experimental results are shown in TABLE 1. If the riser's reactor is used as a benchmark, the product distribution characteristics in the

different reactors are the following:

- **Riser plus a dense-phase bed:** Slightly higher propylene and ethylene yields, but an increasing coke yield of 4.09 wt%
- **Dense-phase bed:** Relatively higher ethylene and propylene yields, but the highest coke yield of 12.24 wt%
- **Fast-fluidized bed:** Moderate light olefin and coke yields
- **Specially configured fast-fluidized bed:** Highest propylene yield of 16.63%, a relatively higher ethylene yield and a moderate coke yield.

**The development of residue-to-chemicals technology.** The co-authors' company has developed a novel residue-to-chemicals (RTC) technology<sup>a</sup> to overcome the defect that DCC technology cannot handle heavier and inferior feedstocks. The essential difference between RTC and DCC is that the riser + dense phase reactor in DCC is replaced by a high-efficiency fast-fluidized bed reactor, as shown in FIG. 3. This RTC technology was successfully commercialized at SINOPEC Anqing Co.'s refinery in January 2020. Compared with DCC, RTC shows good adaptability to inferior feedstock mixed with hydrotreated residue. More importantly, propylene and ethylene can be produced with higher selectivity, while the yields of coke and slurry are reduced.

**Technical features of RTC technology.** RTC technology exhibits higher selectivity for the conversion of heavy oil to light olefins by applying a fast-fluidized bed reactor. The technology has the following technical characteristics:

**Higher catalyst concentration in the RTC reactor.** Most FCC reactors use riser reactors by default, ignoring the effect of catalyst concentration on product distribution. However, catalyst concentration plays the most important role in the production of light olefins in DCC. Since the riser reactor operates in the dilute phase bed, some of the feed molecules that are not in contact with the catalyst undergo unwanted thermal cracking to produce ethylene and methane. In contrast, RTC technology uses a fast-fluidized bed with higher catalyst concentrations than conventional risers. The higher catalyst concentration in the reactor means that the feed molecules have a good chance of contacting the catalyst and that more

propylene can be produced by  $\beta$ -scission.

**Higher temperatures in the RTC reactor.** The pre-lift gas transports regenerated high-temperature catalysts to the bottom of the RTC reactor to mix with preheated feedstocks. Although DCC is an endothermic process, the high concentration of catalysts in the reactor can provide sufficient heat capacity for endothermic cracking. Correspondingly, the temperature gradient from the bottom to the top of the RTC reactor axis does not change much. The entire reactor is kept at high temperatures, which is beneficial to strengthen  $\beta$ -scission to produce propylene and suppress hydrogen transfer in DCC.

**More efficient contact between catalysts and reactants.** Catalytic cracking is a volume expansion process. If the diameter of the reactor remains unchanged, the gas flow velocity gradually increases from the bottom to the top. Severe boundary effects can occur at high central gas velocities. The RTC reactor adopts a special configuration, by which the gas flow velocity along the axial direction of the reactor keeps relatively uniform. Part of the catalyst is refluxed from the boundary to the center of the reactor, enabling more efficient contact between catalysts and reactants.

**A longer stable operation period.** The rear end of the DCC reactor is a dense-phase bed. The outlet oil gas may diffuse into the whole disengager and eventually form coke. The coke thus formed can easily settle and clog the spent catalyst valve, causing the DCC unit to shut down. In contrast, the outlet of the RTC reactor can be directly connected to an enclosed cyclone to prevent oil gas from diffusing into the disengager to form coke. Therefore, RTC has a longer stable operation period vs. DCC.

**Commercial application of RTC technology.** In November 2019, SINOPEC Anqing Co. converted its DCC unit to RTC technology, replacing the original combined reactor of a riser + dense-phase bed with a specially configured fast-fluidized bed. During nearly 2.5 yr of smooth operation, test runs (including varying feedstocks and operating modes) were carried out. All tests have demonstrated an increasing light olefin selectivity and a decreasing coke selectivity for the RTC technology. TABLE 2 details a comparison of the performance of RTC and DCC when treating hydrotreated residue and

**TABLE 2.** A comparison between RTC and DCC in terms of product distribution and gasoline properties

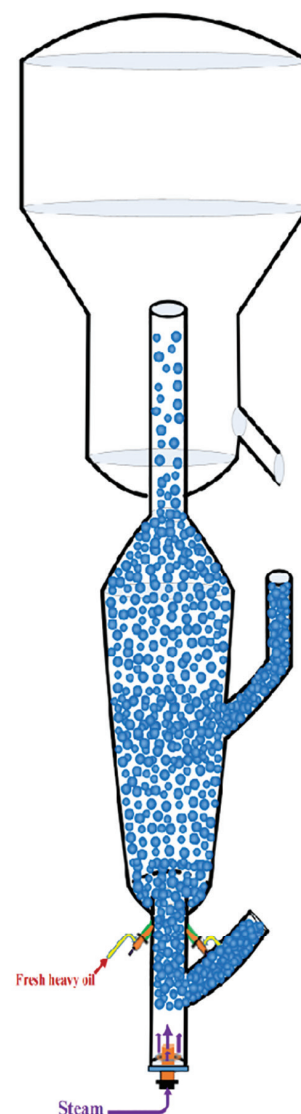
Process	DCC	RTC
Ratio of hydrotreated residue in the feed, wt%	52.67	50.22
<b>Feeds</b>		
Density (20°C, kg × m <sup>-3</sup> )	916	910.6
CCR, wt%	2.65	2.11
<b>Product distribution, wt%</b>		
Dry gas	9.59	9.35
LPG	30.77	34.47
Gasoline	28.43	26.99
Light cycle oil	15.8	14.91
Slurry	6.35	5.83
Coke	8.83	8.27
Loss	0.23	0.18
Propylene yield, %	13.71	16.27
Ethylene yield, %	3.51	4
Ratio of ethylene in dry gas, wt%	36.6	42.79
Ratio of propylene in LPG, wt%	44.56	47.2
RON	97.6	98

VGO blends. Compared with DCC, RTC technology showed an increased ethylene yield of 0.49%, an increased propylene yield of 2.56% and a decreased coke yield of 0.56%. In addition, the mass ratios of ethylene in dry gas, propylene in LPG and the research octane number (RON) of gasoline were improved.

#### Economic benefits of RTC technology.

At the time of this publication, this RTC technology has been licensed to three refineries with a total processing capacity of 12 MMtpy. Another unit, with a processing capacity of 3 MMtpy, will be commissioned in May 2023, and three additional units will be commissioned in 2024. Based on a comprehensive evaluation of product production, product quality and energy consumption, the incremental profit margin of the RTC technology is \$11.94/t of feedstocks vs. DCC technology.

**Follow-up development of RTC technology.** The RTC technology is characterized by the application of a specially configured fast-fluidized bed to intensify  $\beta$ -scission to convert heavy and inferior feedstocks into light olefins. In the further development of RTC technology,



**FIG. 3.** The RTC reactor, consisting of a specially configured fast-fluidized bed.

its feedstock will be expanded to light raw materials such as crude oil, naphtha and diesel, among others. According to industry forecasts, ethylene demand will continue to increase over the next decade. Therefore, it is necessary to increase ethylene yield from the existing 5% to more than 10%, while maintaining an appropriate propylene yield. **HP**

#### NOTES

<sup>a</sup> SINOPEC RIPP's DCC<sup>pro</sup> residue-to-chemicals technology

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## Cut emissions and fuel while increasing capacity in fired heaters

According to a recent digital refining article,<sup>1</sup> fired heaters are responsible for an estimated 400 MMtpy–500 MMtpy of carbon dioxide (CO<sub>2</sub>), with at least 73% of average refinery CO<sub>2</sub> emissions coming from combustion. Refineries and petrochemical plants are under increasing pressure to reduce emissions while also looking for ways to reduce fuel consumption amid rising fuel prices.

Fired heaters have the greatest running cost in a refinery or petrochemical site. If any heater is inefficient by 1%–2%, it can consume an additional \$1 MM/yr in fuel or result in millions of dollars in lost revenue. High fuel consumption also translates to increased emissions. Units of particular interest include catalytic reformers, steam methane reformers (SMRs) and ethylene furnaces.

This article will discuss solutions to issues in the radiant and convection sections of fired heaters that affect performance and profitability.

### RADIANT SECTION EFFICIENCY

Process fluids are heated in the radiant sections of fired heaters. The fluids travel through steel alloy tubes, which are heated principally by radiant heat generated by burners within the refractory lined box. The configuration and condition of the process tubes and the refractory surfaces affect heat transfer efficiency in the radiant section.

**How does process tube oxidation occur?** When used, steel alloy tubes oxidize and scale layers continuously grow on the external surfaces. The developing scale insulates the tube surface, hindering conductive heat transfer to the process and decreasing radiant section efficiency.

Extra heat is needed, and the firing rate

is increased to overcome the insulating effect. This results in increased flue gas temperature (bridgewall temperature). Consequently, CO<sub>2</sub> and nitrogen oxide (NO<sub>x</sub>) emissions are increased. As the scale grows and further increases in firing rate are required, boiler water treatment limitations are encountered and production rates are threatened.

Carburization is an industry trend used to operate fired heaters more efficiently—at lower excess oxygen levels—to save fuel and reduce CO<sub>2</sub> emissions. The increased potential for the carburization of external surfaces of radiant section tubes leads to the grain boundary penetration of carbon, carbide formation, surface embrittlement, crack formation and metal loss. The result is a reduced service life of the radiant tubes.

The author's company offers online tube descaling. This will improve the radiant section heat transfer efficiency and reduce the bridgewall temperature. However, the effect is temporary since oxidation and scale formation will continue.

High-emissivity ceramic coatings provide a protective thin-film layer on the outer surfaces of process tubes, which prevents metal oxidation, corrosion and carburization. This maintains the thermal conductivity coefficient close to new tube conditions. The coatings may be applied to existing tubes during a shutdown or to new tubes at a remote facility where the surface preparation, coating and curing occurs. The average benefit of catalytic reformer heaters is to increase the radiant section efficiency by 6.6%, with a corresponding 6.6% reduction in CO<sub>2</sub> emissions and approximately 20% reduction in NO<sub>x</sub> emissions.

**Refractory surface emissivity: Why does it matter?** A significant portion

of the radiant energy interacts with the refractory surfaces, and the mechanism of this interaction has an appreciable effect on the overall efficiency of radiant heat transfer. A major factor in determining radiant efficiency is the emissivity of the refractory surface.

The ultimate radiant heat transfer efficiency is achieved where the enclosure is a black body, where all the surfaces have the maximum emissivity factor of 1.0.

Ceramic coatings with emissivity values > 0.9 have been designed to supplement the refractory surfaces' radiation characteristics. Benefits of up to 5% in radiant section efficiency improvement with corresponding CO<sub>2</sub> emissions reduction of up to 5% and NO<sub>x</sub> emissions reduction in ethylene and SMR up to 30% can be achieved.



FIG. 1. Heavy fouling on a convection section.



FIG. 2. After-convection section robotically cleaned.



## CONVECTION SECTION EFFICIENCY

**How does fouling occur?** Fouling occurs when deposits accumulate on the tube or fin surfaces. The burner operates with one part per million (ppm) airborne particulates. This means that a single burner can pass 2.5 tpy of debris through a heater, some of which will deposit.

Airborne debris is drawn in from the surrounding environment.

One of the most significant effects of fouling is an increase in emissions. If fouling is left to worsen and the emissions become excessive, refineries may be liable to pay government fines (**FIG. 1**). Fouling requires fired heaters to burn more fuel to operate at the desired capacity—higher fuel consumption results in a higher stack temperature and reduced heat transfer. High operating temperatures cause heat stress on tubes, creating uneven expansion and irregular heat distribution, potentially leading to tube failure. These side effects can cost plants millions of dollars in lost revenue.

Two commonly used offline cleaning methods are used to tackle the issue of fouling: chemicals and dry-ice blasting.

**Chemical cleaning.** Chemicals can be used when an asset is online; however, if the nature of the fouling is unknown, it is difficult to predict how it will react with certain chemicals. Therefore, chemicals can compound the issue of fouling, creating hotspots in areas that the chemical has not managed to penetrate or reach.

During a shutdown, the refractory lining of the convection section can become saturated with water-borne chemicals, which may change the refractory's high-temperature properties, leading to premature failure.

**Dry-ice blasting.** Dry-ice blasting can be undertaken during the unit's operation and is offered by the author's company. It provides a limited benefit since accessibility reduces the ability to reach > 40% of the tube surface area. However, this is often sufficient to provide a significant improvement until a planned shutdown.

The author's company offers a comprehensive solution that uses robotic cleaning systems to clean more than 90% of convection section tube fouling during planned turnarounds (**FIG. 2**).

**Takeaway.** Fired heaters are a critical piece of equipment for refineries and facilities worldwide. With rising fuel costs and stringent emissions legislation, it is becoming increasingly important to ensure that mission-critical assets, particularly fired heaters, perform efficiently and at full capacity.

Maintaining these assets regularly and thoroughly will maintain output, increase asset life, reduce the likelihood of unplanned outages, reduce stack temperatures and emissions, and deliver a significant return on investment. **HP**

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## Combustible dust hazards overview

There has been a significant increase in the use of biomass as alternative energy or green fuel in the last two decades. Biomass comes in many forms and is most commonly used for industrial applications like the fabrication of wood chips or wood pellets for fuel. Wood chips and wood flour are also used to produce chipboard, medium density fiberboard and laminate flooring. The production of these biomass products requires milling, pressing, grinding and other processing techniques that produce fine particulates. In certain configurations, such particulates can present a fire or explosion hazard and must be handled appropriately to prevent catastrophic loss.

The U.S. Occupational Safety and Health Administration (OSHA) has increased its focus on combustible dust hazards. It issued the Combustible Dust National Emphasis Program (NEP) in 2008 due to the number of catastrophic fires and explosions caused by combustible dust over the previous two decades. The NEP describes OSHA's policies and procedures regarding inspecting facilities that handle combustible dust and the administration's expectations regarding owner/operator compliance with U.S. safety standards [e.g., the National Fire Protection Agency (NFPA)].

OSHA has determined that many facilities handling combustible dust were unaware of the associated hazards or were confused by the requirements of the existing commodity-specific standards (e.g., NFPA 61,<sup>1</sup> 484,<sup>2</sup> 654,<sup>3</sup> 664<sup>4</sup> and/or 655<sup>5</sup>), with the NFPA 664<sup>4</sup> standard specifically targeting the wood processing industries. The NFPA, therefore, recently developed and issued the Standard on the Fundamentals of Combustible Dust (NFPA 652<sup>6</sup>), which is a gov-

erning umbrella standard that addresses fire and explosion hazards associated with combustible dust of all types across all industries to promote further awareness and reduce confusion.

A main focal point of NFPA 652<sup>6</sup> is the requirement for facilities that process or handle particulate solids to perform routine dust hazard assessments (DHAs). While several commodity-specific NFPA standards have required a process hazard analysis for more than a decade, NFPA 652<sup>6</sup> goes a step further by making this requirement retroactive for existing installations and establishes a deadline to have a DHA in place. A DHA is now required for new and existing installations and upgrades to existing installations.

The NFPA 652<sup>6</sup> standard, which came into effect on September 7, 2015, allows affected facilities 5 yr to complete a DHA. To put the importance of a DHA in perspective regarding regulatory compliance, the lack of combustible dust hazard analysis is listed as a primary transgression.<sup>7</sup> In addition, recently, a jury awarded \$39.7 MM to a man injured in a fire and explosion at a wood processing facility in 2014. Many of the investigation's findings would likely have been captured in a DHA and could have prevented the incident from occurring.

There are many approaches to conducting a DHA, and the Annex of NFPA 652<sup>6</sup> provides one example. The Center for Chemical Process Safety's (CCPS's) "Guidelines for combustible dust hazard analysis"<sup>8</sup> provides perhaps the most current and comprehensive overview of the different DHA approaches available to a facility. The most common issues identified during many DHAs performed by the author over the last several years are detailed in the following sections. Focus

is given to dust collection systems and associated equipment since such systems are typically present at most particulate solid handling facilities.

### The lack of defined inspection and cleaning plan to meet NFPA housekeeping requirements.

Dust explosions may be classified as either primary or secondary. Primary dust explosions typically occur within individual equipment inside process plants or similar enclosures (baghouse, cyclone, grinder, etc.) and are generally controlled by pressure relief venting through purpose-built ducting. Secondary dust explosions, which are disturbed, suspended and ignited by the primary explosion, result from dust accumulations within facilities but outside of the equipment, resulting in a more dangerous uncontrolled explosion inside the workplace. Loss history shows that most injuries and fatalities from dust explosions result from secondary dust explosions.

Therefore, controlling fugitive dust emissions and housekeeping outside of equipment is a focus of all combustible dust-related standards and is the key to reducing the potential for a catastrophic event. For example, NFPA 664<sup>4</sup> (the wood industry-specific standard) defines a hazardous location as an area where the accumulation of combustible dust exceeds 1/8-in. A hazardous location is deemed to exist if the total area of dust accumulations exceeding the layer depth criterion is greater than 5% of the enclosure footprint area, or if the area of any single dust accumulation exceeding the layer depth criterion is greater than 1,000 ft<sup>2</sup>.

NFPA 652<sup>6</sup> (the umbrella standard) requires that a facility manages dust accumulations to meet the criteria of the relevant commodity-specific standard

(e.g., NFPA 664<sup>4</sup>). Surprisingly, very few facilities create an auditable system of inspection and cleaning to meet this requirement. Some facilities periodically inspect and react accordingly, although local accumulations may already have significantly exceeded the identified threshold thickness within this timeframe. Other facilities simply clean on a defined frequency, regardless of the amount of dust accumulated within this timeframe. Regrettably, some facilities neither inspect for nor clean accumulated dust on any defined schedule.

Although the NFPA standards do not define an approach to achieve compliance, the author's company believes that the most effective method is to segment the process areas into zones that are easily inspected by a workgroup or operator, ensuring no gaps between zones. An initial inspection frequency should be established, and the zone (including elevated surfaces) cleaned as needed when the threshold thickness is approached. For zones that generate dust accumulations at a steady rate, the inspection frequency can be adjusted after a few inspections have established the accumulation rate. The keys to success are maintaining external dust accumulation levels below threshold levels, developing a reasonable inspection frequency, documenting the inspections and cleanings, and making the process

work intuitively without creating an undue burden. An additional benefit to this zoned approach is that the responsible workgroup will likely begin to identify the key equipment contributing to fugitive dust emissions and seek methods to eliminate the source of the emissions (FIG. 1).

#### The lack of dust explosibility data.

Most materials that can combust will present a combustible dust fire and explosion hazard if dust is created from processing such materials. Dust generated from combustible material should be assumed to pose a combustible dust fire and explosion hazard unless proven otherwise. However, beyond identifying a combustible dust hazard, a facility often does not have sufficient information on the combustibility characteristics of its dust.

Performing a simple Go/No-Go test is fundamental to confirm that a hazard exists. Once the determination is made that the dust is combustible, additional explosivity parameters may be useful to quantify the hazard and develop effective mitigation options. For example, knowledge of the minimum explosible concentration may be necessary to determine if the process can generate enough airborne dust to present an explosion hazard. Likewise, knowledge of the minimum ignition energy is essential when determining the potential for static ignition hazards, which may require operators to be bonded/grounded when performing certain operations.

For the most part, this information is well established for the variety of wood species processed in industry. However, particle size and moisture content play a significant role in ignition sensitivity and explosibility severity characteristics. These parameters obviously will vary depending on the type of wood processed, the process involved (e.g., sander, rip saw, computerized numerical control) and locations in the process where dust concentrations are greatest (e.g., dust collectors). Having the correct data is essential to appropriately evaluate the hazards and associated risks of the process.

**The lack of rated deflagration isolation device.** NFPA standards state isolation devices should be provided where an internal explosion hazard exists to prevent deflagration propagation between connected equipment. Without isola-

tion, an explosion initiated in one piece of equipment could propagate to connected equipment. In addition to allowing the explosion to propagate, this also results in pressure piling in the downstream equipment, which can significantly increase the explosion pressures. The connected equipment could fail even if protected with a suitable explosion protection system (e.g., explosion vent). Another concern is exposing personnel working near dust collection duct pick-up points or hoods (e.g., bagging and hand-dumping operations) to the flame propagating through the connecting duct.

Many varieties and manufacturers of deflagration isolation devices are often sold as flame-front diverters, fast-acting check valves, backblast dampers or backdraft valves. Many observed installations would not function as intended due to a poor valve mating surface (i.e., would not prevent flame propagation) or a weak housing that would not withstand the deflagration overpressure generated in the connected equipment. The EN 16447 ATEX standard<sup>9</sup> is the only international testing protocol that evaluates these devices under actual blast conditions to ensure they will function properly over the relevant explosibility parameter range. When selecting a deflagration device, always ensure the device meets the ATEX certification and that the device is rated for the explosibility characteristics (e.g.,  $K_{ST}$ ,  $P_{max}$ ) of the dust being handled. NFPA 69<sup>10</sup> guides implementation and other considerations relative to isolation devices.

**Lack of restricted access zones around equipment equipped with deflagration vents.** Restricted occupancy zones must be established around deflagration vents to reduce the likelihood that personnel are in the vicinity if a deflagration occurs in the vented equipment. Several incidents have injured personnel located near explosion vents due to exposure to the flame and burning debris from the vented deflagration. Equipment controls and e-stops should be located outside of these zones. NFPA 68<sup>11</sup> provides guidance on fireball distances from vented enclosures that can be used to establish restricted access zones.

Of course, locations right at the edge of the fireball are not necessarily safe due to the high thermal flux; hence, an addi-



FIG. 1. Example of poor housekeeping.



FIG. 2. Firefighter caught in a vented dust deflagration fireball. (Photo courtesy of OSHA.gov)

tional safety distance should be considered (FIG. 2). Restricted zone warning signs and barriers should be established to prevent unauthorized personnel access. Permits should be used to evaluate potential hazards encountered by personnel working within the restricted zone, specify appropriate personal protective equipment and limit the time to which personnel are exposed to this hazard.

### Lack of design basis information to support explosion protection design.

When designing and implementing explosion protection systems, it is imperative to know the strength of the protected equipment. For example, the maximum explosion pressure in equipment fitted with explosion vents can significantly exceed the pressure at which the vents open, and the equipment may fail catastrophically if not designed to withstand the maximum pressure. Similarly, if chemical suppression is implemented, the activated suppression system pressurizes the equipment as it injects the suppressant, and hence the equipment will fail if not designed appropriately.

In one instance, the author's company assessed the capacity of a rectangular baghouse with an explosion suppression system and determined that the baghouse would fail at the roof-to-shell seam without additional structural reinforcement (FIG. 3). Activation of the suppression system, even inadvertently, posed a significant hazard to the operators.

**The lack of design basis system flow velocities.** NFPA standards prescribe minimum flow velocities through dust collection systems to prevent dust from falling out of suspension and accumulating inside the duct. Dust accumulations can lead to a hidden fuel source that may be ignited by a spark drawn into the system. Duct fires can present a challenge to extinguish and often can damage equipment beyond repair. In some cases, the burning material can be pulled into the dust collection system and initiate a deflagration. Maintaining a minimum flow velocity of 4,000 fpm is recommended by NFPA standards to prevent the fallout of dust in dust collection ductwork—the actual required velocity is a function of the dust properties. In some cases, facilities have created peepholes in the ductwork into which a flowmeter can be periodically introduced to monitor the flow velocity and validate system integrity. Intelligent dust collection systems are also available that include in-line flow velocity sensors that control the fan speed to maintain the minimum designated velocity and balance the system when sections are taken out of service.

### The lack of duct inspection hatches.

The placement of inspection hatches along the dust collection system duct allows for periodic inspection for dust accumulation, although the NFPA standards do not explicitly require such hatches. The author's company recommends that inspection hatches are located the equivalent of approximately 20 duct diameters along the main duct. This criterion may be different for individual small-diameter trunks sprouting from the main duct. Regardless of specific inspection hatch spacing, the intent is that all sections of the ductwork can be inspected and cleaned sufficiently through the hatches.

### Spark suppression system nozzles located too far from the spark source.

Dust collection ductwork connected to high-frequency spark generating equipment (e.g., sander, grinder, hog) should be equipped with a spark suppression system to minimize or eliminate sparks entering the dust collector, which could trigger a collector fire or deflagration. The spark suppression system typically incorporates a sensor (i.e., infrared, rate of pressure rise) that detects the spark, along with spray nozzles located downstream at a distance determined by flow velocity. The separation distance between the detector and suppressors is critical: too close and the spark may get beyond the spray before it is activated; too far and the spray may halt before the spark arrives. The location of the spark suppression system is also critical. The FM Global Loss Prevention Data Sheet 7-76<sup>12</sup> recommends that the system be as close to the final piece of spark-generating equipment as possible. Otherwise, if dust has accumulated in the duct between the spark-generating equipment and the spark suppression system, such accumulations can be ignited. Of course, spark suppression systems only reduce the likelihood of ignition, and additional explosion protection is required.

It is also noted that NFPA standards

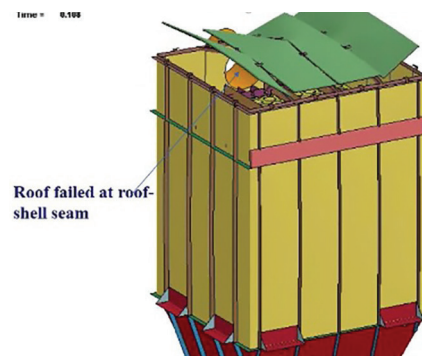


FIG. 3. Failure of baghouse roof-to-shell seam under suppression injection pressure.

require that horizontal ductwork be capable of supporting the weight of the system plus the weight of the duct half-filled with water (where sprinkler protection is provided in the duct) or the material being conveyed, whichever has the higher density. The author's company knows at least one case where a large duct collapsed due to water accumulation from fire suppression activities.

**Takeaway.** The identified common hazards have all been causal factors in actual combustible dust fire or explosion incidents that resulted in the loss of life or severe injury, in addition to the loss of capital assets and business interruption. Performing a robust DHA should identify these hazards and, using the guidance provided in relevant NFPA standards, determine prevention and mitigation strategies that can be implemented to manage the risk associated with combustible dust fire and explosion hazards. **HP**

### LITERATURE CITED

- <sup>1</sup> NFPA 61, *et al.*, "Standard for the prevention of fires and dust explosions in agricultural and food processing facilities," 2020.
- <sup>2</sup> NFPA 484, *et al.*, "Standard for combustible metals," 2022.

Complete literature cited available online at [www.HydrocarbonProcessing.com](http://www.HydrocarbonProcessing.com).



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## Hot oil pump warm-up system best practices and failure case study

Many industries utilize pumps in hot applications, including oil and gas facilities. Pump manufacturers and end users consider the pump warm-up system configuration to be an essential consideration during pump design, manufacturing and commissioning stages. The scope of this article focuses on typical guidelines and best practices for hot applications where warm-up systems are required for proper startup and reliability of the pump. These warm-up systems are designed to bring the pump up to a uniform temperature in a controlled manner before it is started, and to maintain the standby pump at uniform process temperatures to allow for auto-start.

However, there is a different train of thought per recent guidelines from API RP 682, which is that pumps handling fluids with operating temperatures greater than 150°C, or those handling high-pour-point fluids, should utilize a warm-up system to obtain and maintain the appropriate pump operating temperature. Pump manufacturers typically provide specific recommendations for

warm-up system requirements, based on different pump configurations. The following outlines four primary considerations to monitor during a pump warm-up process to prevent damage to the machine and/or the mechanical seal(s).

**Heating rate.** A controlled heating rate is required to minimize temperature gradients that can produce non-uniform thermal expansion, resulting in compromised internal clearances and subsequent pump damage and/or seizure of the rotating element. The original equipment manufacturer (OEM) will provide a recommended heating rate based on the type and size of the pump. In the absence of guidelines from the manufacturer, a typical rule of thumb for the heating rate is as follows:

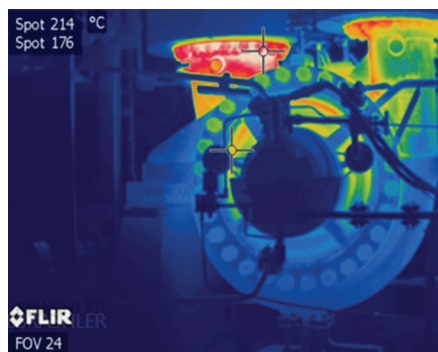
- Maximum heating rate of 50°C/hr (122°F/hr) up to 260°C (500°F)
- Maximum heating rate of 25°C/hr (77°F/hr) above 260°C (500°F).

**Thermal shock.** Another important consideration for a pump's warm-up procedure is to avoid thermally shocking the pump and associated components by rapidly introducing hot fluid to it. Thermally shocking the pump may result in significant damage or failure, including the mechanical seal faces. Typically, startup procedures mandate a commissioning of the mechanical seal support system prior to initiating the warm-up process.

**Thermal stratification.** Another important consideration is thermal stratification, which can occur when pumps are not warmed up properly. Fluid density differences due to changes in fluid tem-

perature can result in a thermo-siphoning effect, with the hotter fluid at the top of the pump casing and cooler fluid migrating to the bottom of the casing. The uneven thermal expansion of the casing and the rotating element can result in galling of the rotating and stationary components and/or complete seizure of the rotor. Higher vibration amplitudes can also be expected due to the internal misalignment created by this condition. **FIG. 1** shows an infrared thermal signature of a pump casing with this uneven temperature profile across the pump casing. Notice the top-top suction and discharge nozzles—this condition can occur when there are no warm-up lines located at the bottom of the pump casing.

**Pump startup temperature.** A final consideration for a successful pump warm-up and startup is related to startup temperature. The startup of a pump prior to reaching the required startup temperature can result in damage to internal running clearances and/or mechanical seals. The pump should be ready to start when a pre-specified temperature margin is established relative to the product or operating temperature. This specified temperature margin will vary with the pump design and the nature of the pumped fluid, and these guidelines are typically provided by the pump designer. This can be particularly important for fluids with a high pour-point temperature or for fluids that solidify at temperatures below normal operating temperature. In the absence of any guidelines or specific requirements from the pump's OEM, the recommended guideline is that pump startup should not occur until the cas-



**FIG. 1.** Thermal signature showing an uneven temperature distribution.



ing temperature is within 40°C (104°F) of the operating temperature and the pump has experienced a heat soak at that temperature for a minimum of 2 hr. FIG. 2 shows the same pump casing's thermal signature; however, the thermal signature now clearly indicates that there is a uniform temperature distribution across the entire casing (top to bottom).

**Typical warm-up system design.** A typical warm-up system piping and instrumentation diagram (P&ID) for the subject design—which is a double-suction, radially split between bearing, top-top nozzle configuration—is shown in FIG. 3. As shown in this case, there are three warm-up lines, each entering the pump bottom casing drains. A multi-stage orifice is also utilized to effectively break down the high pressure and provide the required warm-up flowrate to satisfy warm-up criteria.

### CASE STUDY: PUMP FAILURE

Three process areas are classified as hot service applications at one Saudi Aramco Red Sea refinery. Each process area utilizes a 3 × 50% pump configuration with an API BB2 radially split between bearing design. The pumps are driven by an induction motor and utilize an API Plan 54 mechanical seal support system. The hot service applications are outlined in TABLE 1, which details service, process temperature and operating philosophy.

**Observed failures.** Multiple failures were observed with these pumps during the first 3 mos of commissioning. The main failure modes observed were related to mechanical seal failures and galling of internal running clearances, as outlined below:

1. The process fluid solidified, leading to a compromised hydraulic balance line and a subsequent loss of axial thrust balance. This condition also over-pressured the sealing chamber, resulting in contamination of the API Plan 54 seal support system. Subsequently, the entire central barrier skid system supplying the main process pumps was contaminated.
2. The pump was started with a blinded warm-up line without meeting the previously specified criteria, resulting in the seizure

of the rotor at the balance line/sleeve location (FIG. 4).

The investigation team performed a thorough assessment to analyze the pump failure modes and provide recommendations to improve reliability and prevent reoccurrence. The primary findings of the investigation were related to warm-up system deficiencies, as outlined below:

- All hot service pumps have no thermal insulation, which can affect both the warm-up rate and the effectiveness of the overall warm-up process.
- Improper warm-up line restriction orifice sizing resulted in compromised warm-up conditions.
- A lack of a proper warm-up of the standby pump was due to a normally closed discharge valve that was motor operated. The normal location for the warm-up line take-off is between the discharge valve and the check valve.
- There was no permissive to start controls to prevent startup of the pump without proper thermocouple temperature readings.
- Generic warm-up procedures did not meet the required warm-up procedure that was recommended by the pump vendor and also specified on the P&ID. Often with new installations, the P&IDs are

developed prior to awarding the pump designer. This can lead to discrepancies in what is represented on the P&ID and the actual requirements of the pump designer.

### Key takeaways and best practices.

Hot pump applications require special considerations in terms of design and operation. It is important to understand the recommended warm-up procedures for a particular pump design to ensure a reliable startup and operation of the pump. The following outlines some of the considerations and best practices for hot pump applications:

- Pump casing thermocouples should be used to ensure uniform warm-up of the pump and to verify that all criteria have been satisfied for a successful startup. This temperature instrumentation can also be used to configure

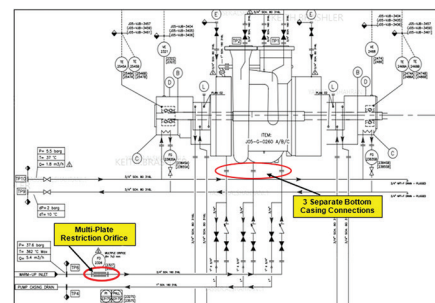


FIG. 3. View of typical warm-up system flowlines and restriction orifices.

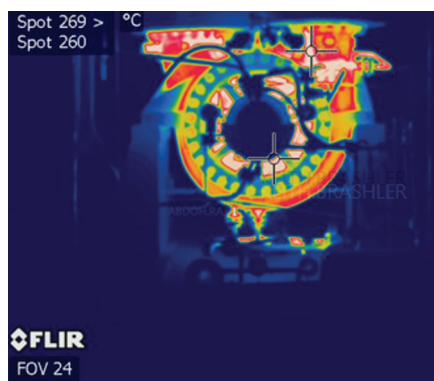


FIG. 2. Thermal signature showing a uniform temperature distribution.



FIG. 4. View of the seized rotor at the balance line/sleeve.

TABLE 1. Hot service applications at a Saudi Aramco refinery

Process description	Process temperature, °C (°F)	Operating philosophy
Vacuum residue pumps	362 (684)	Two running + one spare (3 × 50%)
Atmospheric residue pumps	357 (675)	
HVU LCR pumps	306 (583)	

a permissive to start function, which provides a safeguard from starting the pump without proper warm-up conditions.

- Infrared thermography can also be utilized to provide a clear indication of the heat distribution across the entire pump casing. This technique will avoid issues, such as thermal stratification, that installed casing thermocouples may not indicate.
- Specific or customized warm-up procedures should be developed for each application, avoiding generic warm-up procedures. This is especially important with pump designs such as multi-stage configurations between bearing and top-top pump nozzle configurations.
- As per API 686, warm-up lines should be provided with sufficient flanges to allow the piping spool between the pump and the discharge check valve to be removed and/or aligned independently from the warm-up

line. This will also protect the small-bore piping during the rigging.

- Utilize one NPS 1-in. or larger bypass line around the discharge check valve. A restriction orifice is typically used to establish the required warm-up flow, and often requires a multi-stage orifice to break down the high pressure from the discharge side of the pump and to control the flowrate.
- For all double-suction and multi-stage pumps, a minimum of two independent warm-up lines are required. One bypass line around the discharge check valve and additional warm-up lines are connected to the bottom casing drains.
- Warm-up lines should be heat traced and insulated if the fluid will solidify at lower temperatures. Insulation also provides a safety element related to burn hazards.
- The pump suction valve should be maintained open, unless the warm-up line is isolated—

otherwise, the pump suction valve and piping will be subjected to full discharge pressure. **HP**

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